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Nano Chemical Sensor Development

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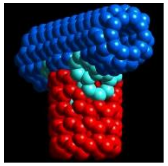
What Do We Expect from a Well-Designed Chemical Sensor System?



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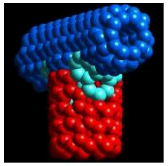
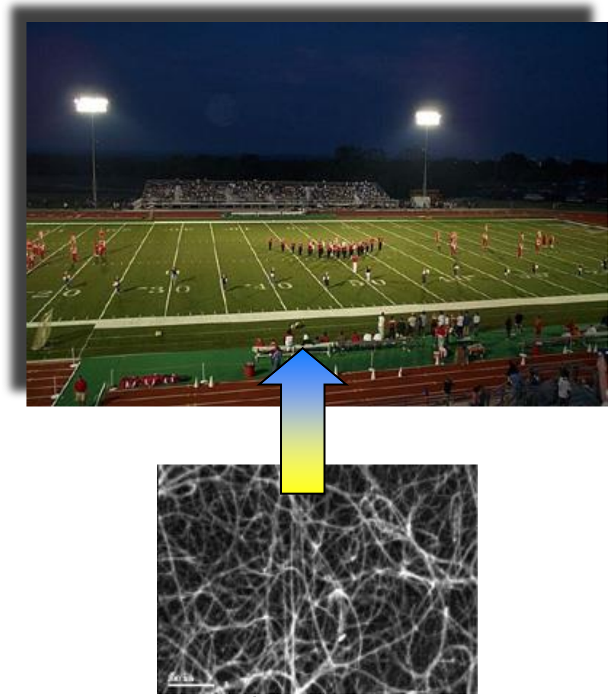
- First, a single device has no value. We need a system consisting of:
  - Sensor array (Electronic Nose, Pattern recognition…)
  - Pre-concentrator?
  - Sample delivery, Microfan? Jet?
  - Signal processing chip
  - Readout unit (data acquisition, storage)
  - Interface control I/O
  - Integration of the above
- Criteria for Selection/Performance
  - Sensitivity (ppm to ppb as needed)
  - Absolute discrimination
  - Small package (size, mass)
  - Low power consumption
  - Rugged, reliable
  - Preferably, a technology that is adaptable to different platforms
  - Amenable for sensor network or sensor web when needed

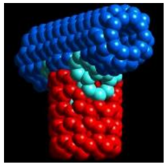
Why Nanomaterials/Nanosensors?



- Compared to existing systems, potential exists to improve sensitivity limits, and certainly size and power needs
- Why? Nanomaterials have a large surface area. Example: Single-walled carbon nanotubes (SWCNTs) have a surface area ~1600 m^2/gm which translates to the size of a football field for only 4 gm.
- Large surface area → large adsorption rates for gases and vapors → changes some measurable properties of the nanomaterial → basis for sensing
  - Dielectric constant
  - Capacitance
  - **Conductance**: our choice
  - Deflection of a cantilever
  -

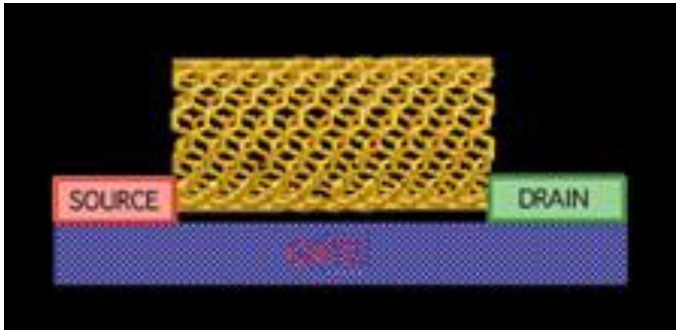


4 grams

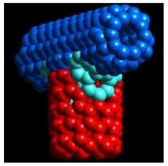


Conductivity Change of CNTs upon Gas/Vapor Adsorption

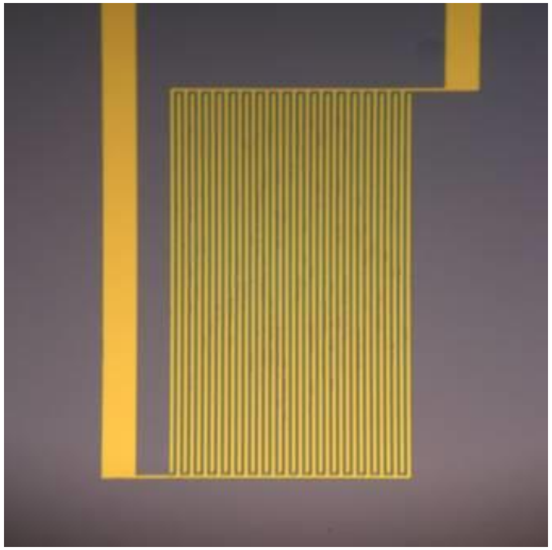
- Early chemical sensors were of the CHEMFET type with SnO_2 and other oxide conducting channels as we have seen before.
- Similar CNT-FETs have been tested in the literature, exposing to NH_3, NO_2, etc.; change in conductivity has been observed (Kong et al., Science, Vol. 287, 2000)
- Limitations of CNT-FET
  - Single SWCNT is hard to transfer or grow *in situ*
  - Even a film of SWCNTs by controlled deposition in the channel is complex
  - 3-terminal device is complex to fabricate
  - Commercial sensor market is very cost sensitive

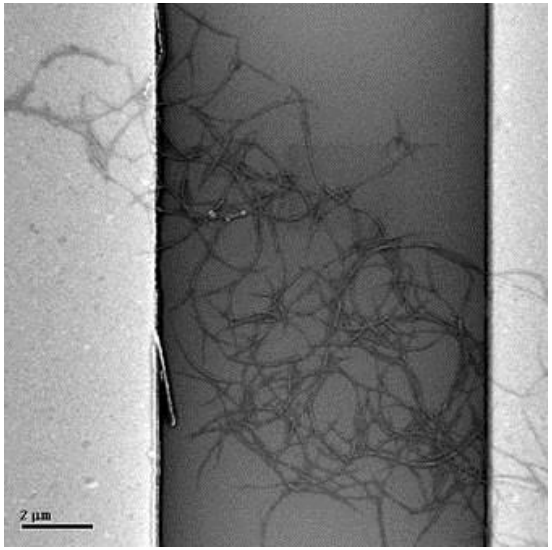


SWCNT Chemiresistor



- Easy production using simple microfabrication, compared to FETs
- 2 Terminal I-V measurement
- Low energy barrier - Room temperature sensing
- Low power consumption: 50-100 µW/sensor



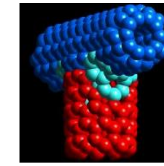


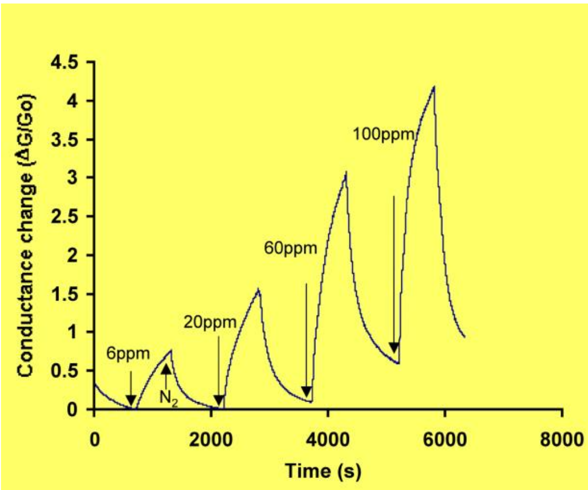
Processing Steps

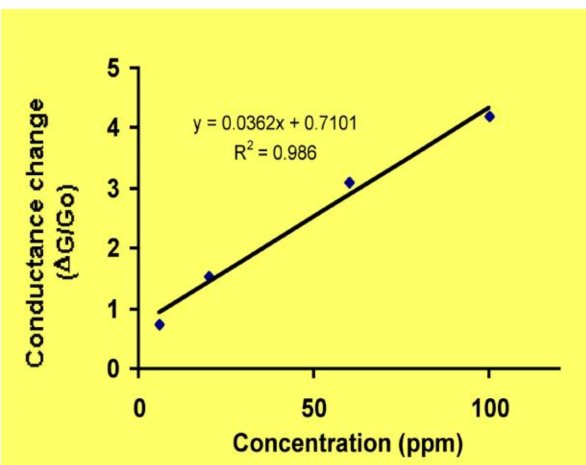
1. Interdigited microscale electrode device fabrication on silicon wafer
2. Disperse purified nanotubes in DMF (dimethyl formamide)
3. Solution casting of CNTs across the electrodes
3. After solvent evaporates, a thin film of CNTs bridges the electrodes; strong adhesion.

Jing Li et al., Nano Lett., **3**, 929 (2003)

SWCNT Sensor Testing and Training
An Example for NO_2 Detection





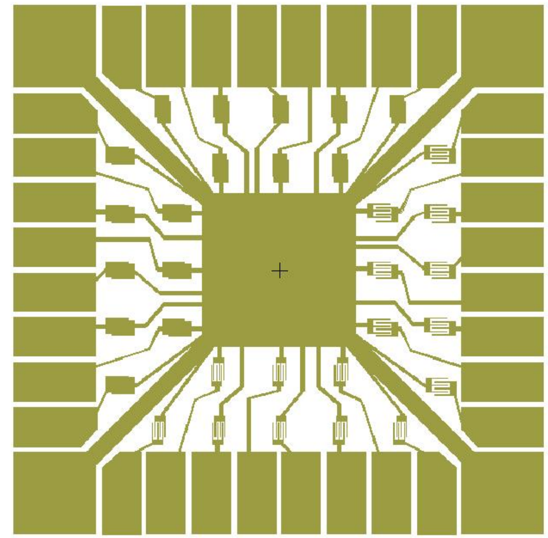


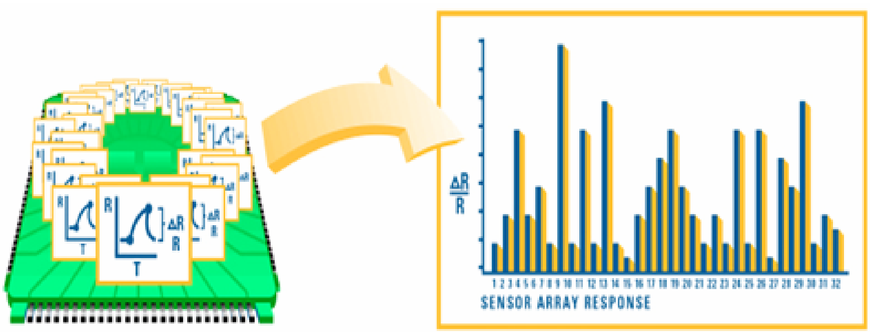
Detection limit for NO_2 is 4 ppb.

- Test conditions:
  Flow rate: 400 ml/min, 23 ^oC
  Purge & carrier gas: N_2 or Air
- Measure response to various concentrations, plot normalized conductance change vs. concentration
- Sensor recovery can be speeded up by exposing to heating, UV light or AC bias
- Full recovery to baseline is not critical during operation as we only look for a change in slope triggered by any event.

Nanosensing Approach: Selectivity

- Use of a sensor array (32-256 sensors)
- Variations among sensors
  - physical differences
  - coating
  - doping
  - nanowires



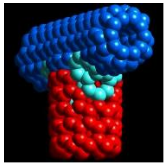


Using pattern matching algorithms, the data is converted into a unique response pattern

<u>Operation:</u>

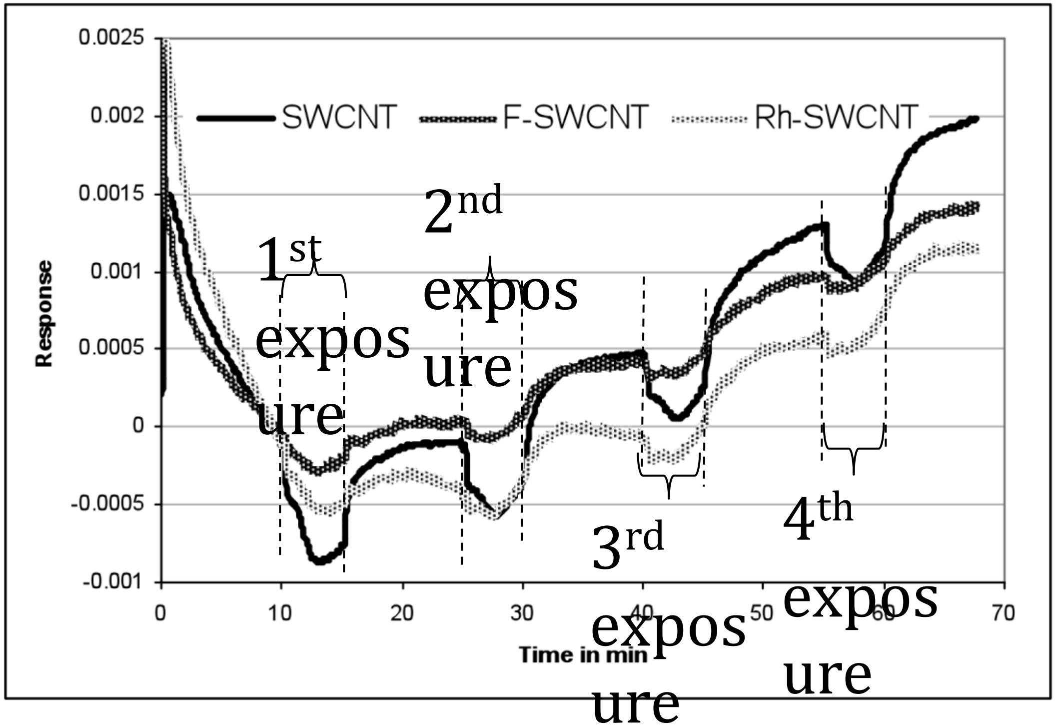
1. The relative change of current or resistance is correlated to the concentration of analyte.
2. Array device “learns” the response pattern in the *training* mode.
3. Unknowns are then classified in the *identification* mode.
4. Sensor can be “refreshed” using UV LED, heating or purging

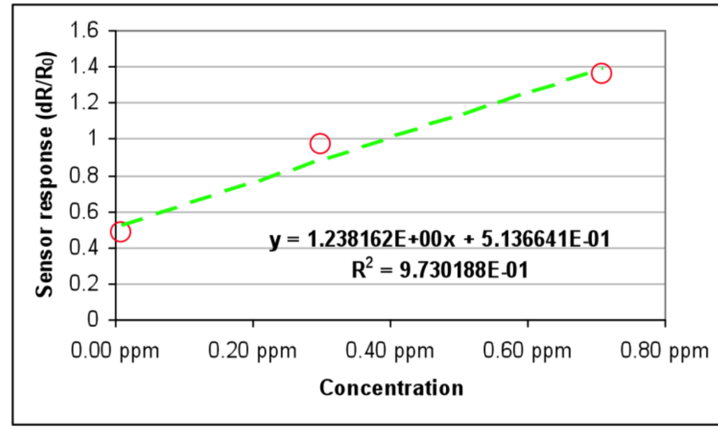
Gases/Vapors Tested

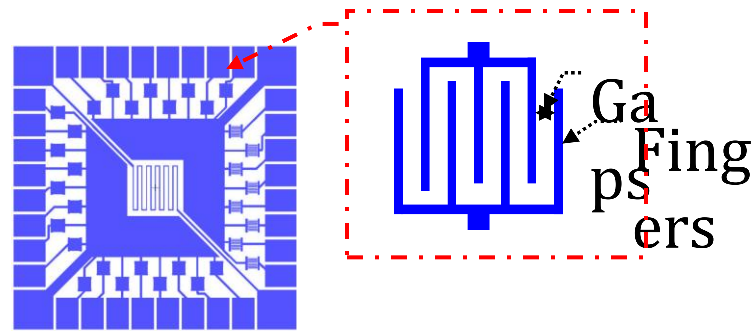


Analyte	Sensitivity/Detection Limit
CH_4	1 ppm in air
Hydrazine	10 ppb tested by **KSC**
NO_2	4.6 ppb in air
NH_3	0.5 ppm in air
SO_2	25 ppm in air
HCl	5 ppm in air
Formaldehyde	10 ppb in air tested by **JPL**
Acetone	10 ppm in air
Benzene	20 ppm in air
Cl_2	0.5 ppm in air
HCN	10 ppm in N_2
Malathion	Open bottle in air
Diazinon	Open bottle in air
Toluene	1 ppm in air
Nitrotoluene	256 ppb in N_2
H_2O_2	3.7 ppm in air
DMMP	100 ppb in air

Detection of Formaldehyde







- Pristine, Rh-loaded and PEI-functionalized SWCNT: all give fast response ~18 seconds
- Recovery time ~1 min
- Detection limit: 10-20 ppb

Hydrogen Peroxide Trace Detection

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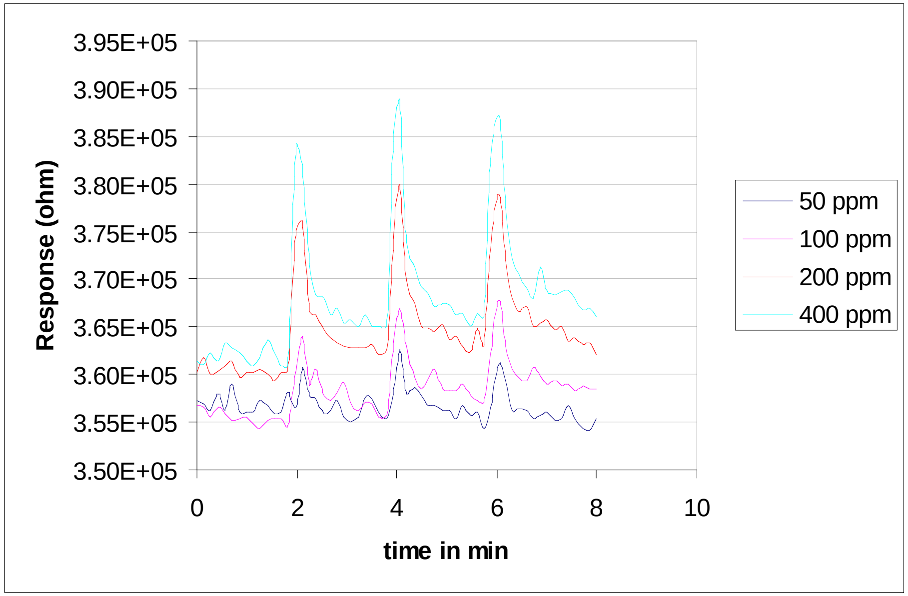

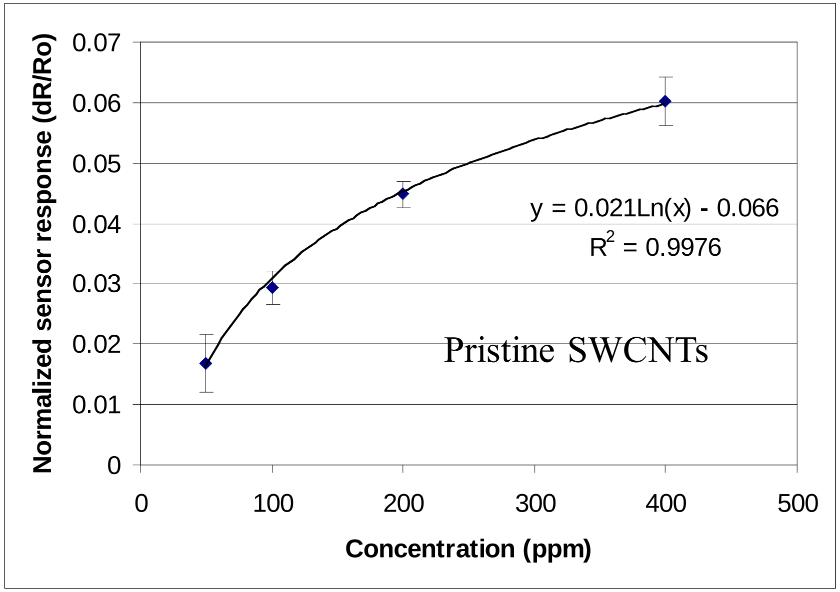

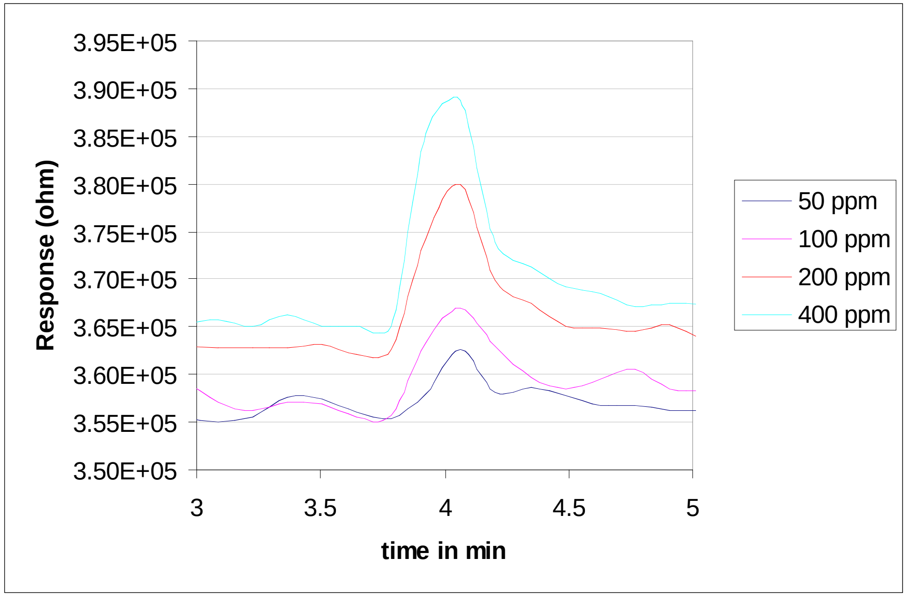

H_2O_2

- Widely used industrial chemical
- Possibility of extant of life based on a mixture of water and oxidizer like H_2O_2
- Ingredient in liquid explosives and home-made explosives
- OSHA limit is 1 ppm, weighted as an 8-hr average

Discrimination between H_2O_2 and Water or Alcohol

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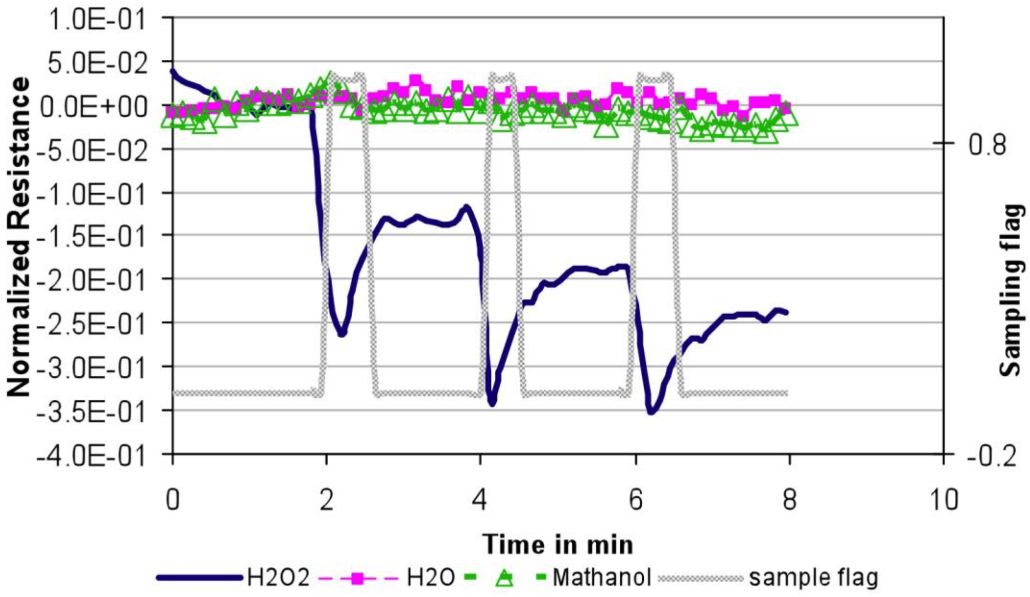


polyethyleneimine (PEI)-functionalized SWCNTs

- Headspace test: sensor exposed to open bottles of H_2O_2, water, and methanol
- Substantial difference in responses
- Adequate to construct e-nose with 32-sensor elements

H_2O_2

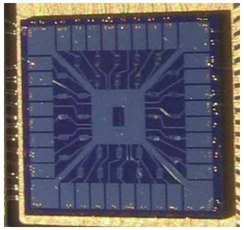
- Fast sensor response: 6 seconds
- Detection limit: 25 ppm

Mechanisms?

•Electron donation from an oxidizer like H_2O_2 decreases the conductivity of the inherently p-type SWCNTs in air

•PEI-functionalized SWCNTs have been shown to be n-type. Their conductivity increases after exposure to H_2O_2

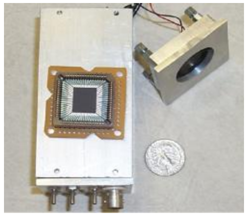
Gas Sensor Platforms to date

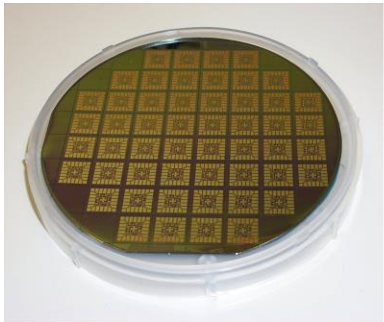


1 cm^2

4”

5” x 5”





Features:

- Response time in seconds
- ppm/ppb detection levels
- Multichannel chip provides high sensitivity/ multifunctions
- Integrated Temperature, Pressure, and Humidity sensing
- Integrated signal processing
- Low power demand (50 mW including all operations)
- Low cost microfabrication

- **12 to 256 sensing elements on a chip (1cm x 1cm) with heater.**
- **Number of sensing elements can be increased on a chip.**
- **Number of chips can be increased on a 4” wafer.**
- **Wafer size can be increased to 6”, 8”, or 12”.**
- **SWCNT solution-casting by ink jetting or using microarrays**

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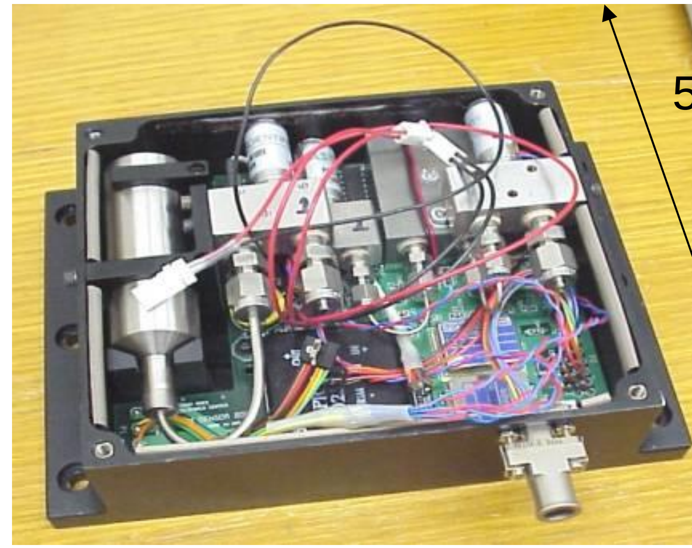
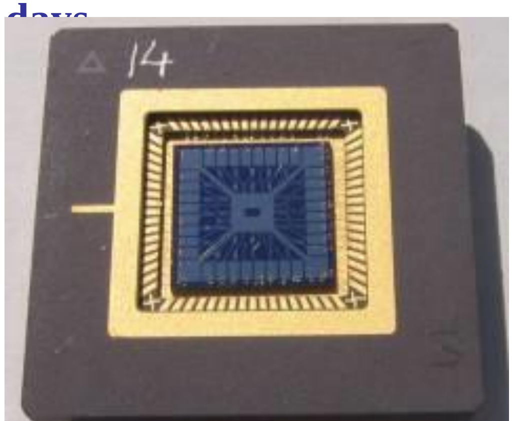
First Nano Product in Space

NASA Ames chemical sensor module was on a secondary payload of a Navy satellite (Midstar-1) launched via Atlas V on March 9, 2007. Sensor data downloaded for 60 days.



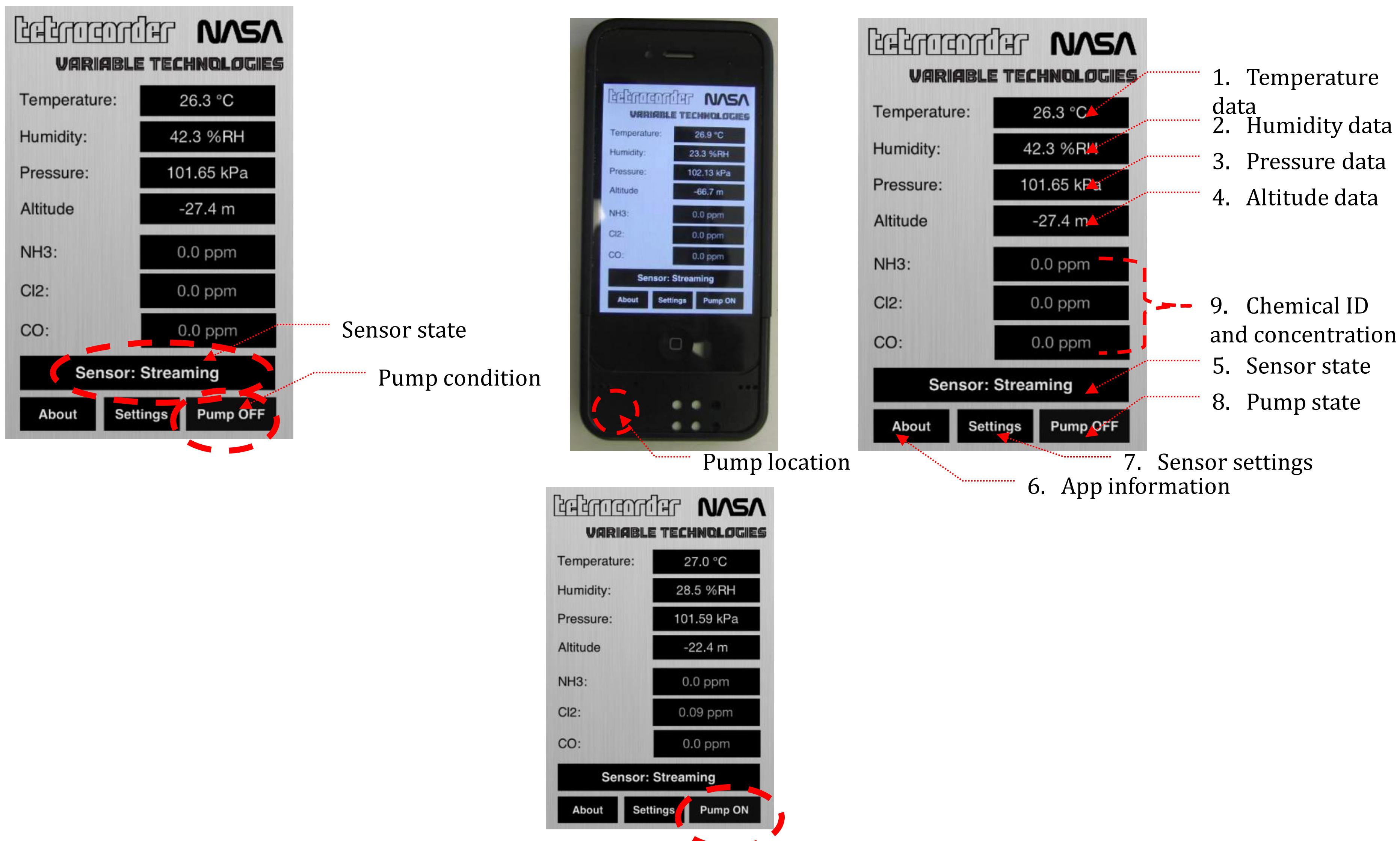
The nanosensor module (5”x 5”x 1.5”) contained a chip of 32 sensors, a data acquisition board, sampling system, and a tank with 20ppm NO_2 in N_2.



A 32-channel sensor chip (1cm x 1cm) with different nanostructured materials for chemical sensing

This sensor chip was intergrated in the JPL E-nose aboard the International Space Station in January 2009 to monitor air quality in the crew cabin, especially formaldehyde.

Chemsensor on the Cell Phone



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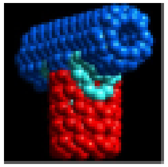
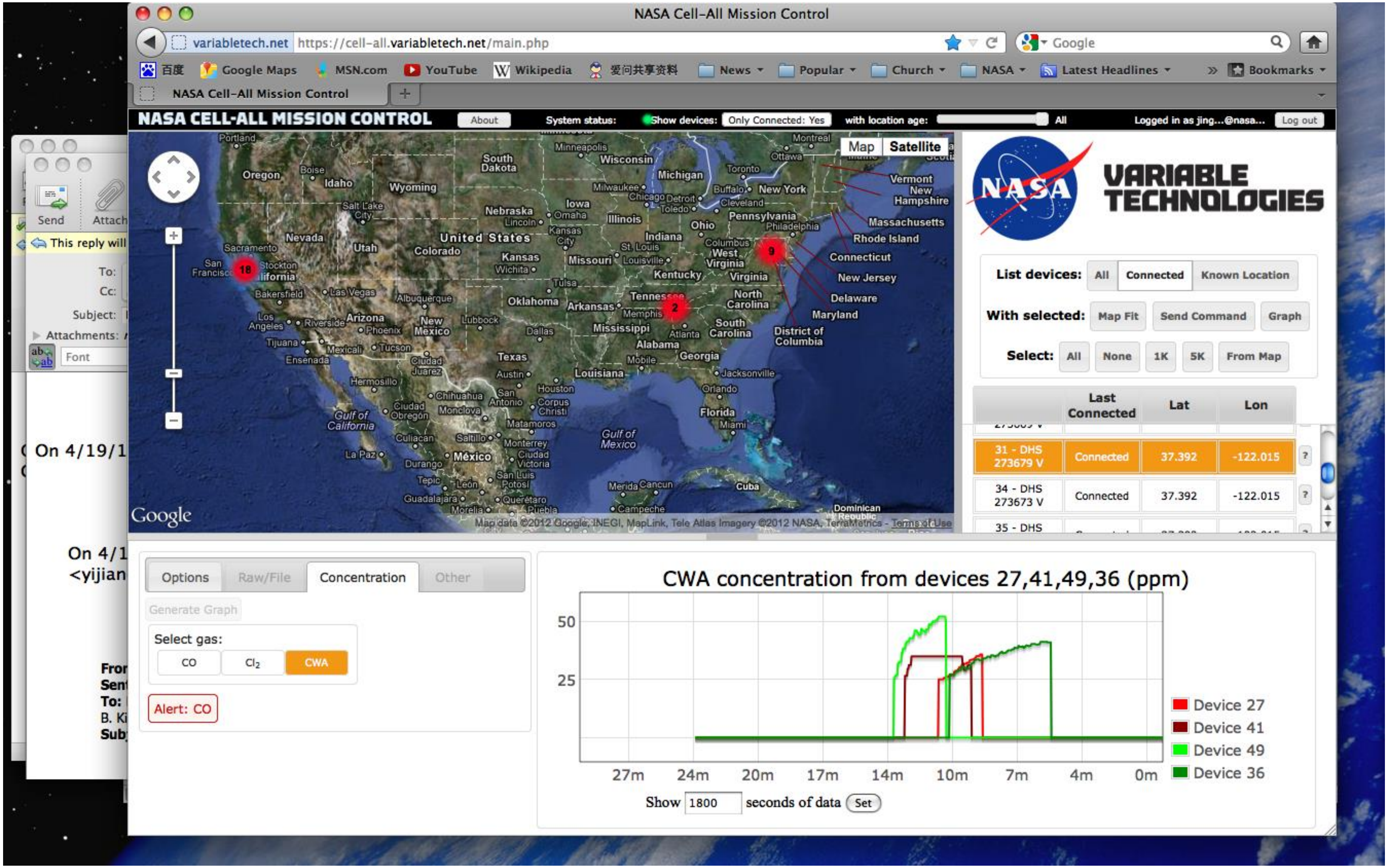
Cell Phone Sensor Network





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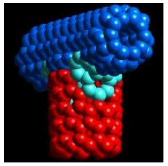
Summary of our Nanochem Sensor



- Currently at TRL 5-6; took us 10 years to get here with an investment of over $ 10 M from NASA, DHS and DTRA
- Flight tested twice: 1. launched on a Navy Satellite in 2007 aboard an Atlas V rocket; detected NO_2 supplied *in situ* from a small tube and reproduced ground test data; telemetry over 60 days. 2. launched on JPL electronic nose in Jan 2009 to International Space Station.
- US Army AMRDEC has independently tested our sensors to monitor the air space around missiles to monitor ageing and reliability issues. Sensor reproduces data from analytical instrumentation
- NASA KSC has tested the Sensor for hydrazine leak detection
- Dept of Homeland Security funded development of a cell-phone version of this sensor. DHS independently tested the sensor for undisclosed chemical threats in an undisclosed location in Alabama and informed us of the success. DHS also arranged for Los Angeles Fire Department test the cell phone sensors for CO detection in a public event in 2011.