

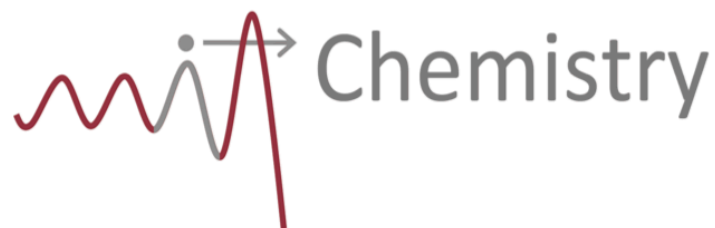
Carbon Nanotube Based Chemical Sensors



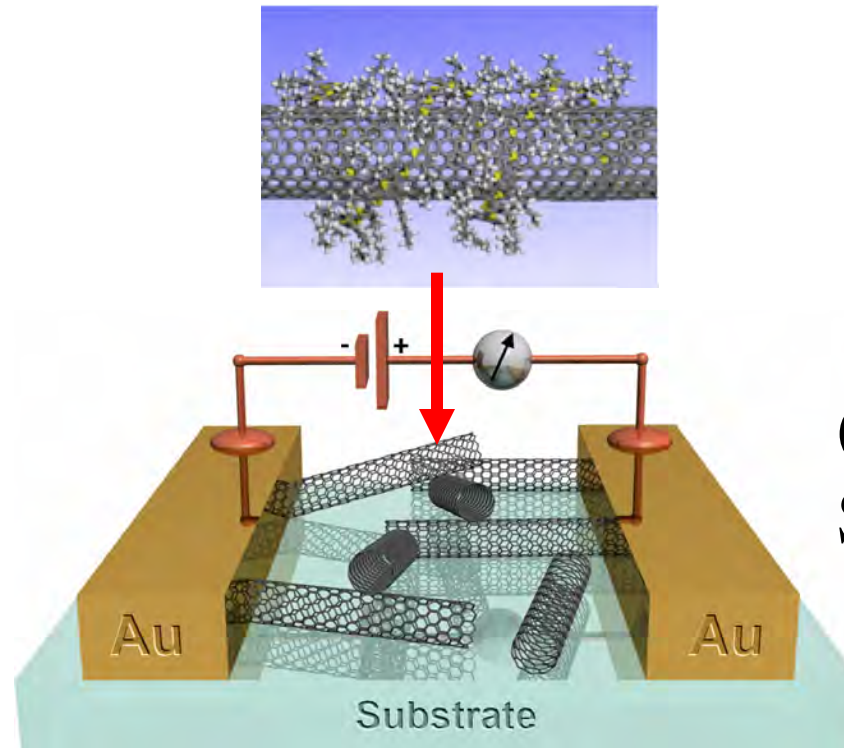
MIT ILP Conference, Tokyo Japan

January 26, 2018

Timothy M. Swager



CNT Chemiresistors



(+) p-Doped (air)
Semiconductors

Advantages

Low Power/Cost
Small Footprint
Wireless Network

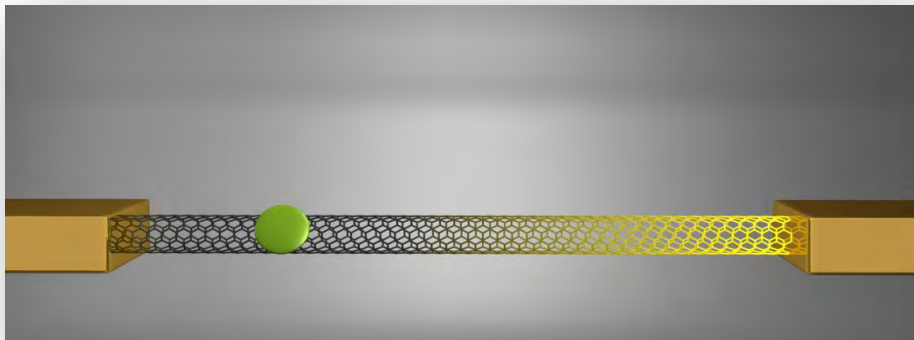
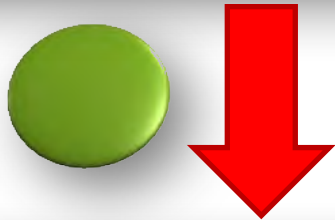
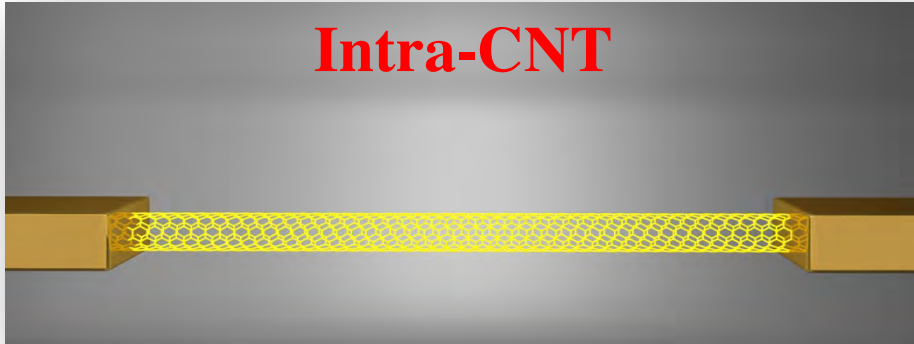
Technical Needs

High Sensitivity
Selectivity
Minimize Drift

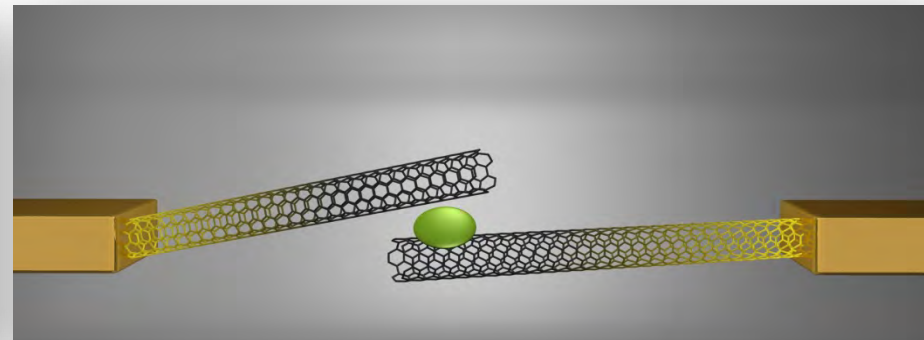
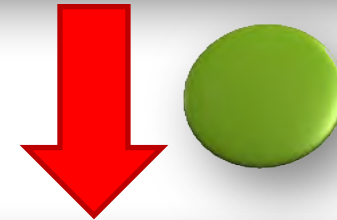
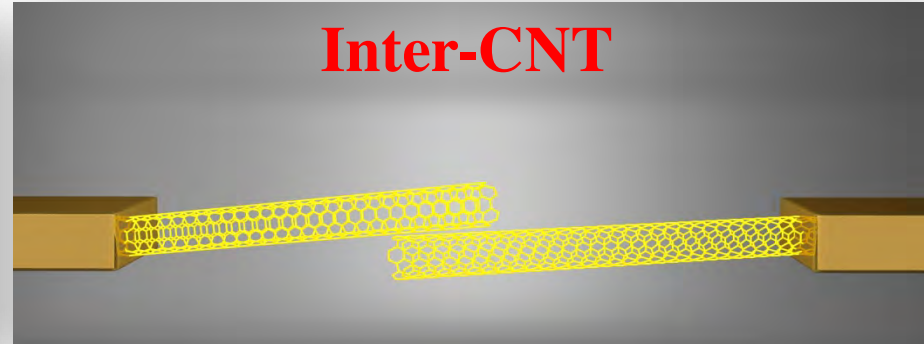
Carbon Nanotube Sensing Mechanisms

Chemiresistor/Chemicapacitance Responses are Often the Result of a Complex Mixture of Mechanisms

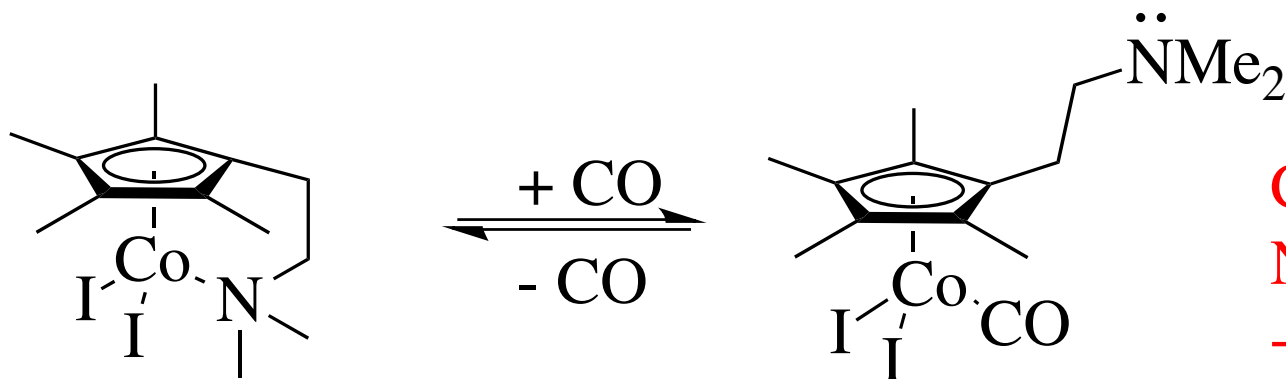
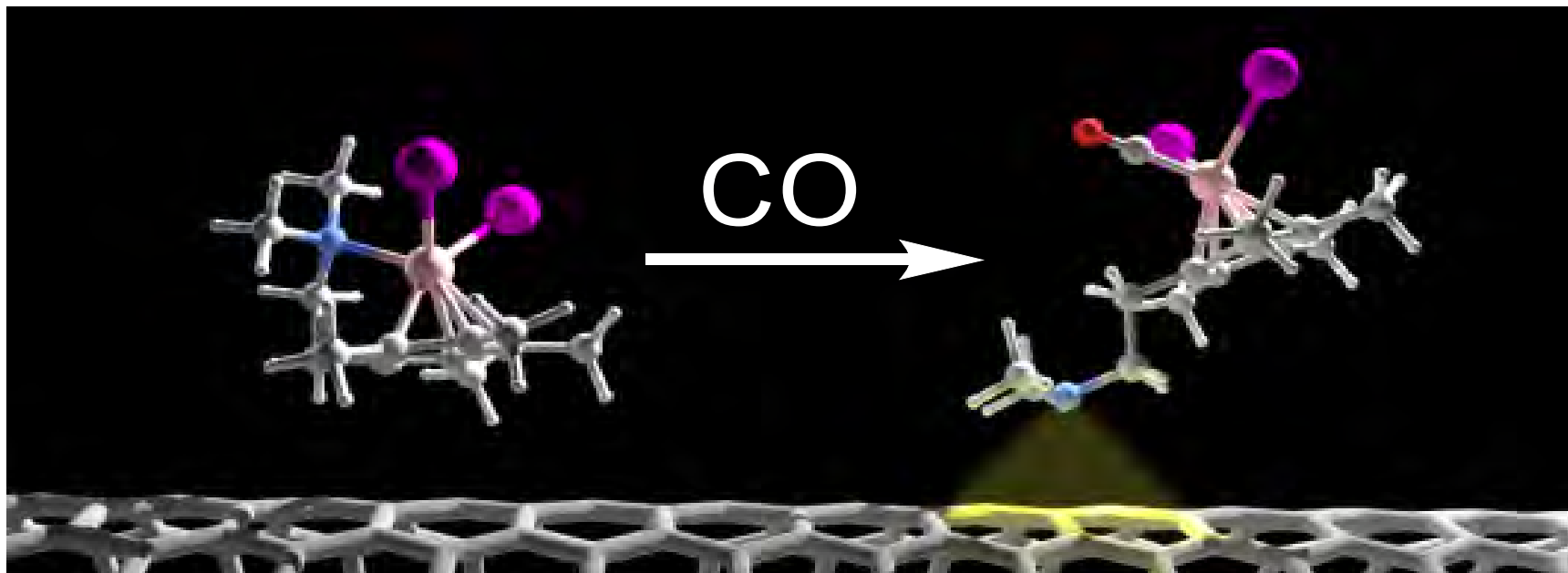
Intra-CNT



Inter-CNT



Triggered Amine Release

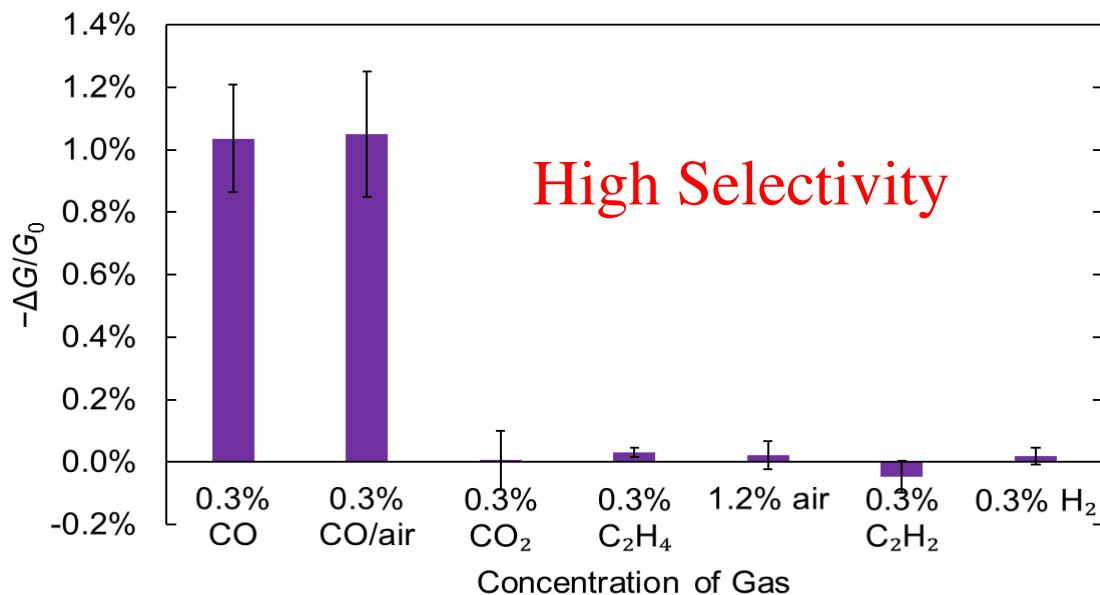
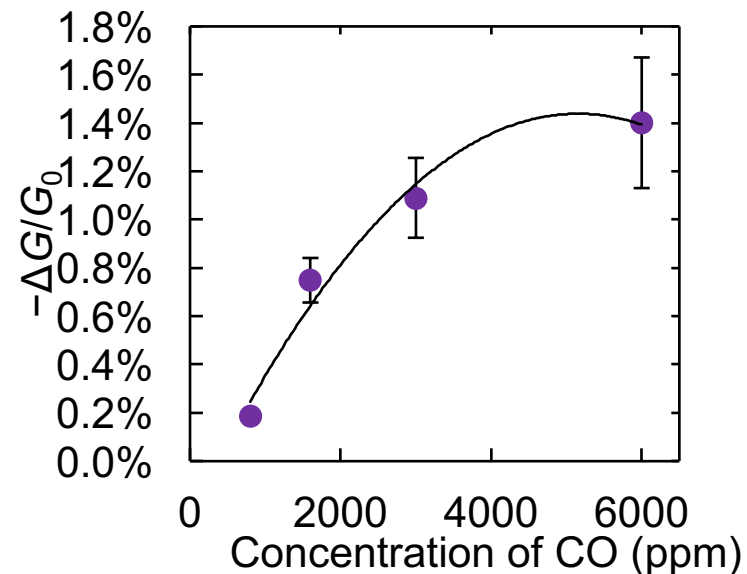
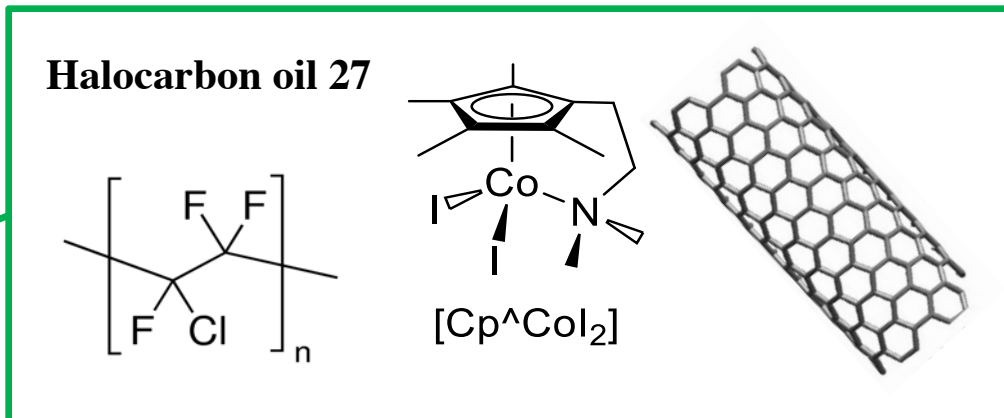
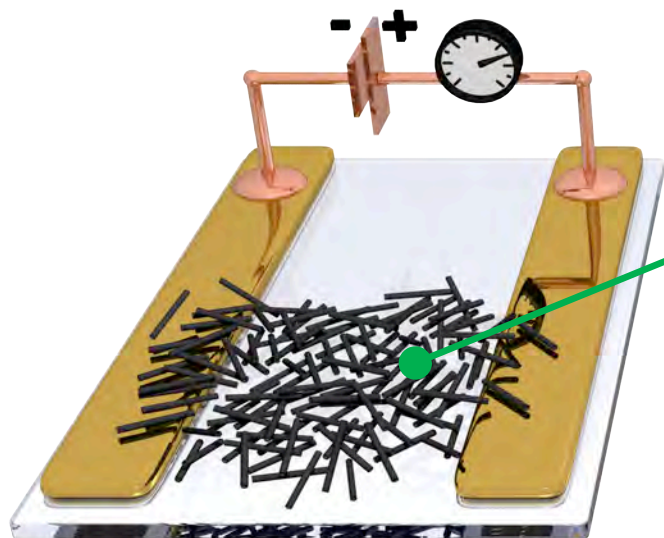


Charge Transfer to the
Nanotube Reduces the
+ Carriers (Holes)

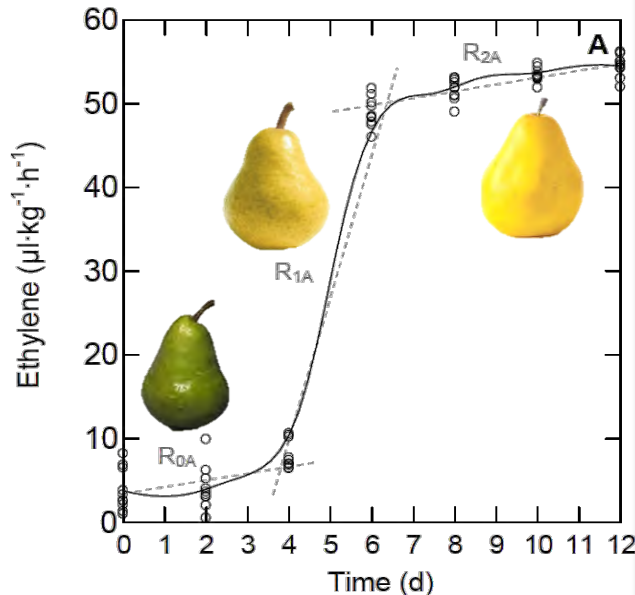
Liu, S. F.; Lin, S.; Swager, T. M. *ACS Sensors* **2016**, *1*, 354-357

Jutzi, P.; Kristen, M.; Dahlhaus, J.; Neumann, B.; Stammer, H.-G. *Organometallics* **1993**, *12*, 2980-2985.

[Cp[^]CoI₂]-CNT Chemiresistors



Gases in Food Management



Ethylene emission increases close to peak ripeness

Ethylene:

- **Given off by produce during ripening** (15+ climacteric fruits, e.g. avocado, banana, apple, mango)
- **Induces ripening** (35+ fruits, vegetables, and flowers respond to ethylene)
- **Indicator of plant health** (can be combined with measurement of other gases)

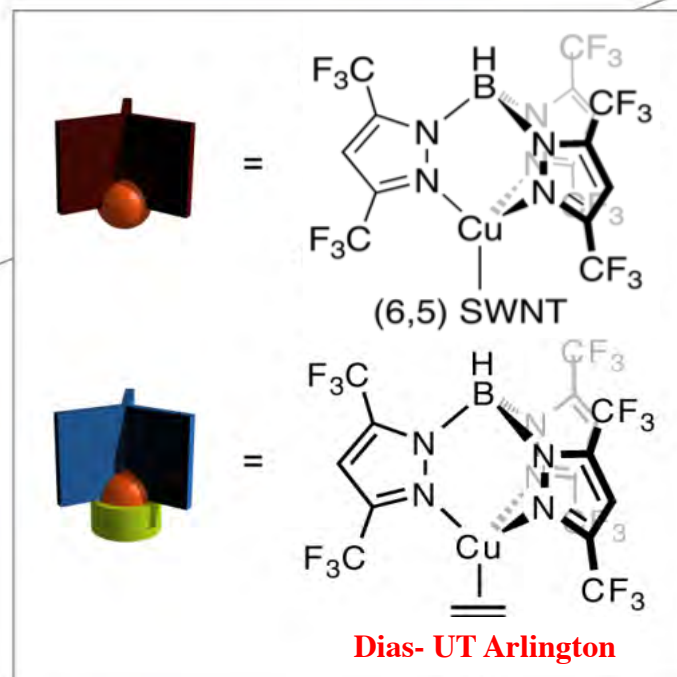
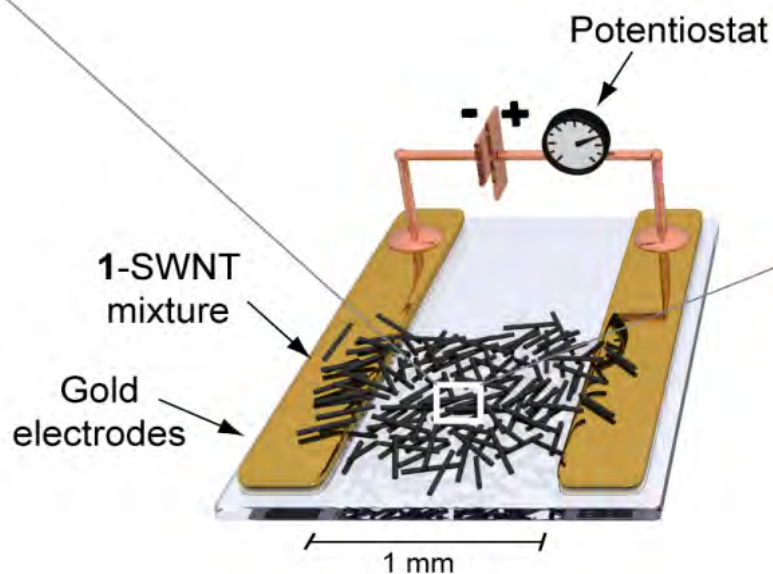
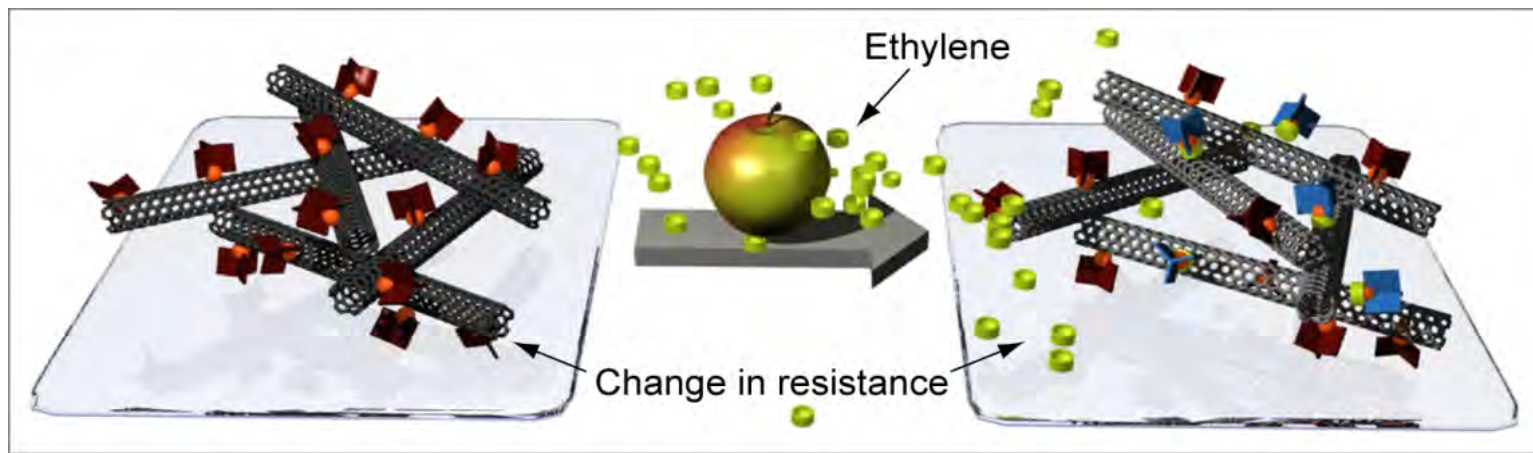
Amines:

- **Indicator of meat/fish spoilage**

Ammonia:

- **Soil nutrient level monitoring**

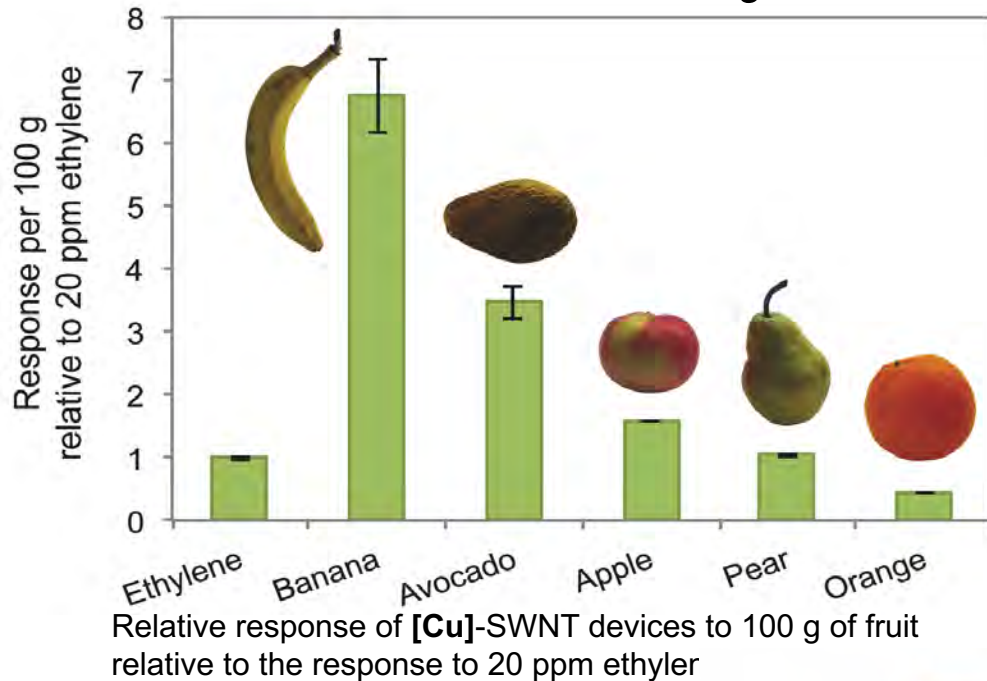
SWCNT-Based Ethylene Chemiresistors



Birgit Esser and Jan Schnorr

Angew. Chem. Int. Ed. **2012**, *51*, 5752-5756.

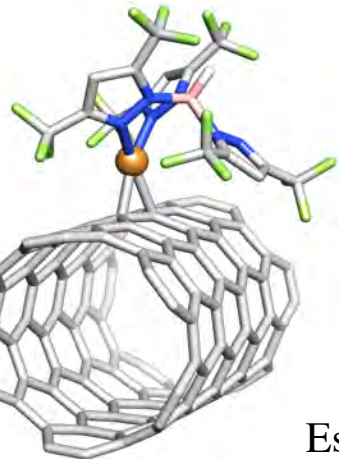
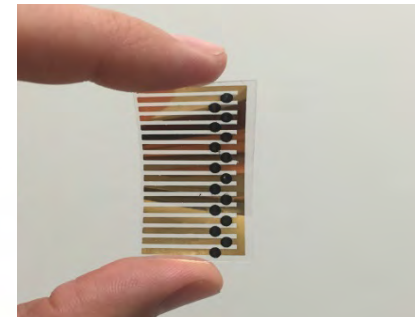
Detection of Ethylene Emissions from Fruit



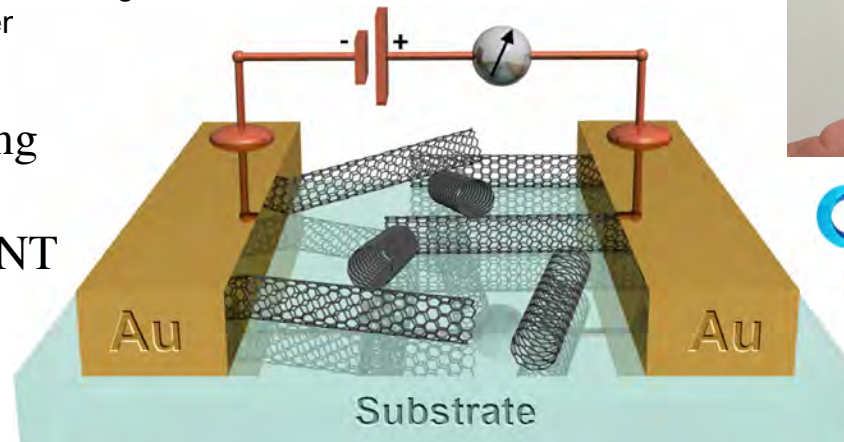
Carbon Nanotube Chemiresistors

- **Plug and Play:** variable resistor read-out
- **Array-Capable:** 80+ analytes demonstrated
- **Miniature:** 1-2 mm² per sensor element
- **Low cost:** replaceable sensor chips
- **Disposable:** paper, plastic, or glass substrates
- **Simple Fabrication:** screen- or inkjet-printing

Sensors on Plastic



Ethylene Binding
Metal Complex
Bound to SWCNT

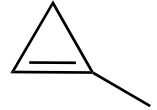


Real-Time Ethylene and 1-MCP Sensors for Apple Cold Storage Rooms

Pilot Product Deployed at
100+ Locations in 12
Countries

AgroFresh

FOR IMMEDIATE RELEASE



1-methylcycloprop-1-ene

AgroFresh Introduces Novel Sensor Technology

New sensors pair with SmartFresh™ technology to provide unparalleled peace of mind to storage room operators

PHILADELPHIA, Sept. 7, 2016 – AgroFresh Solutions, Inc. (NASDAQ: AGFS) and **C₂Sense, Inc.** have co-developed proprietary sensors to monitor ethylene and 1-methylcyclopropene (1-MCP), the active ingredient in patented SmartFresh™ post-harvest technology. The sensors are designed to deliver real-time information for better insights into the condition of fruit in refrigerated and controlled atmosphere (CA) storage rooms.



Apple Cold Storage Facilities: \$1M in Each Room



Protecting Plants in Greenhouses



Ethylene Sources



Ethylene:

- Given off by produce during ripening
- Induces ripening/spoilage

Protecting Plants in Greenhouses



0 0.01 0.1 1 10

Ethylene Concentration ($\mu\text{L}\cdot\text{L}^{-1}$)

Current Ethylene Sensor

Ethylene:

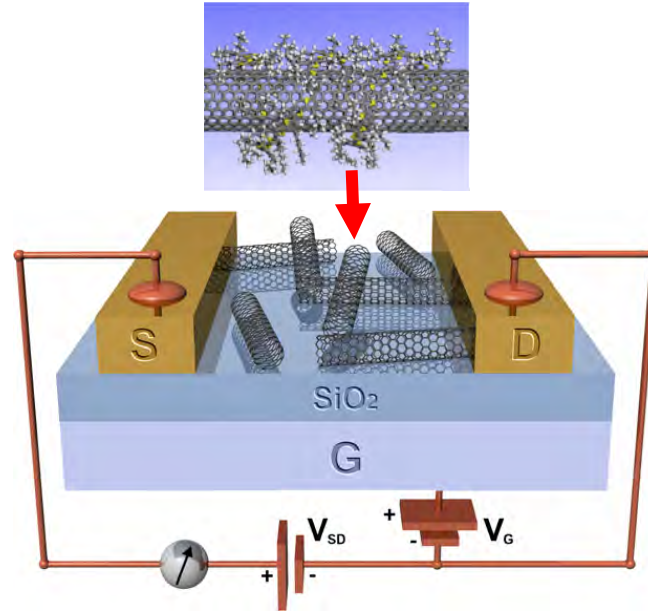
- Given off by produce during ripening
- Induces ripening/spoilage

Better
Option



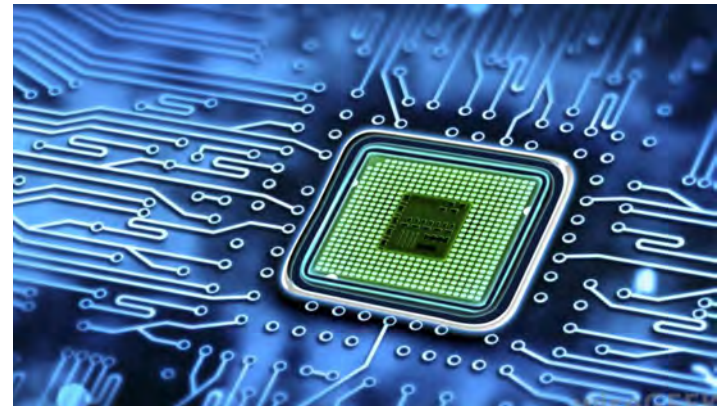
CNT Chemiresistors

Sensor Arrays



Technical Need
Minimize Drift

Plug and Play with Complex
Integrated Circuit Technology to
Provide Massive Diversity and
Redundancy



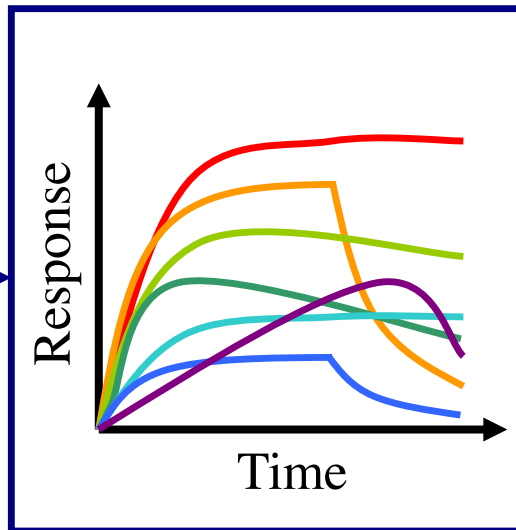
Sensing with Cross Reactive Arrays

Real time measurement

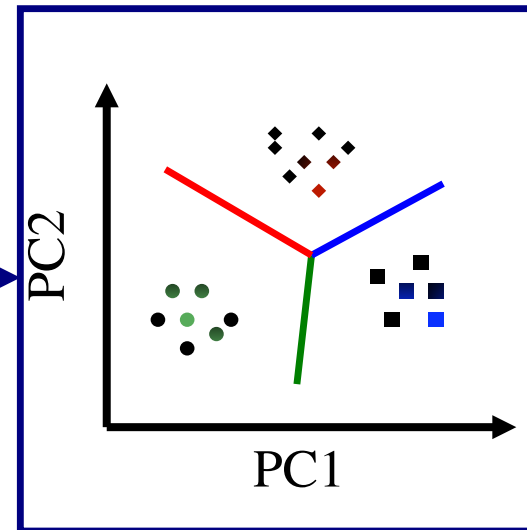
Statistical treatment



Sensor array



Raw data



Classified data in reduced dimension

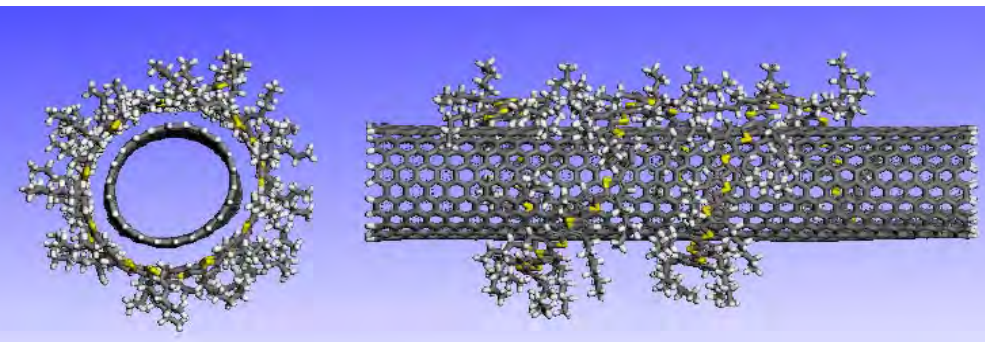
Need Very Stable Sensors and Selectivity is Necessary!

Chem. Rev. 2000, 100, 2595–2626

Cross-Reactive Chemical Sensor Arrays

Keith J. Albert,[†] Nathan S. Lewis,^{*,‡} Caroline L. Schauer,[†] Gregory A. Sotzing,[‡] Shannon E. Stitzel,[†] Thomas P. Vaid,[†] and David R. Walt^{*,†}

Functionalization: Covalent vs. Noncovalent



Noncovalent:

Minimal Effect on the Electronic Structure

Key for Single Walled Carbon Nanotubes

J. Am. Chem. Soc. **2008**, *130*, 5392

Angew. Chem. Int. Ed. **2008**, *47*, 8394

Angew. Chem. Int. Ed. **2010**, *49*, 95

Covalent:

Robust Connections

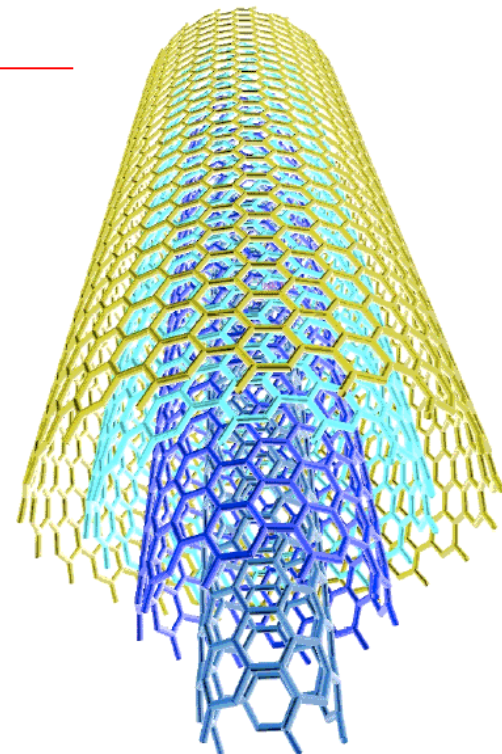
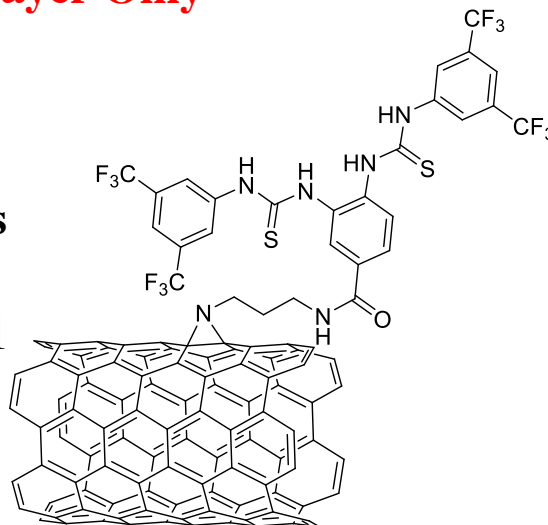
MWCNTs Functionalization Outer Layer Only

J. Am. Chem. Soc. **2011**, *133*, 11181

Sparse Functionalization of SWCNTs

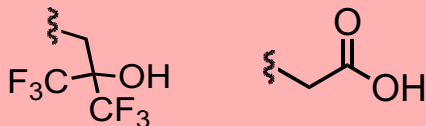
Minimizing Effects on Conductance

Adv. Funct. Mater. **2013**, *23*, 5285-5291



Dissecting Chemical Space for Array Sensing

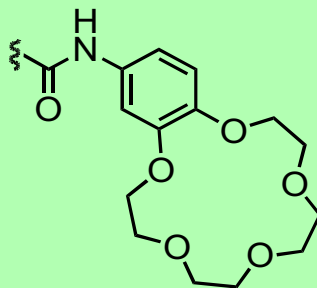
H-bond donor



Ethers, ketones

H-bond acceptor

(with polarity)



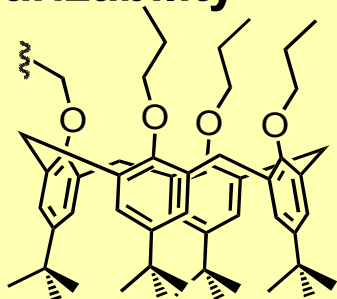
Acids, alcohols, water

Polarity

C=O from cycloaddition chemistry

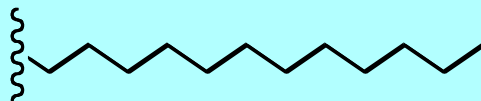
Vapor with high polarity such as acetone.

Polarizability



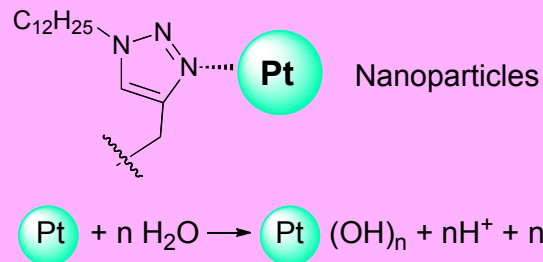
Aromatic and chlorinated hydrocarbons

Nonpolar adsorption



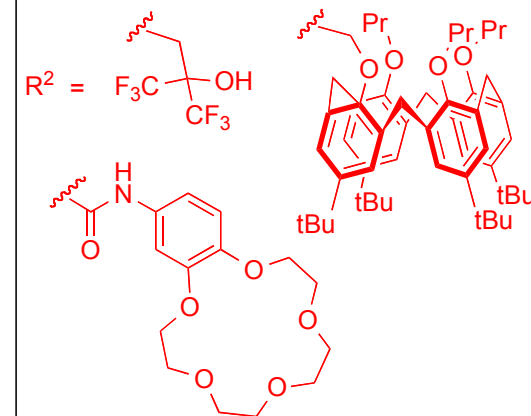
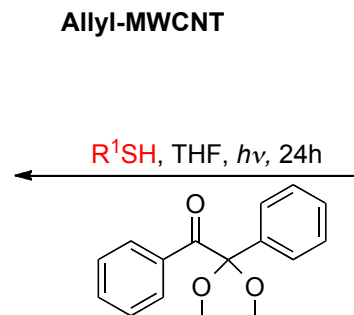
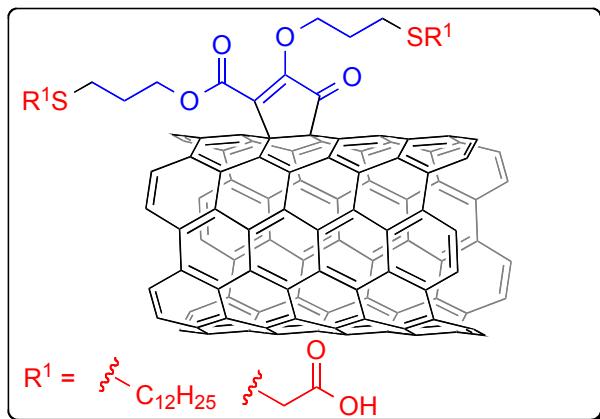
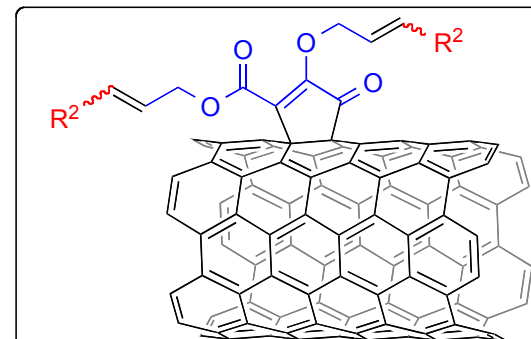
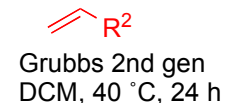
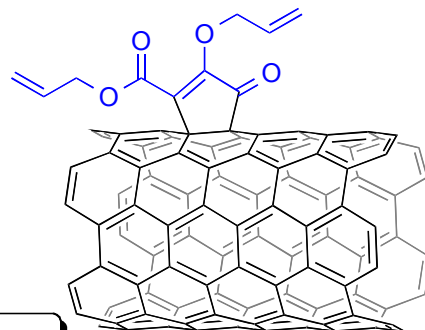
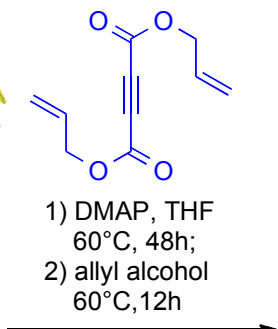
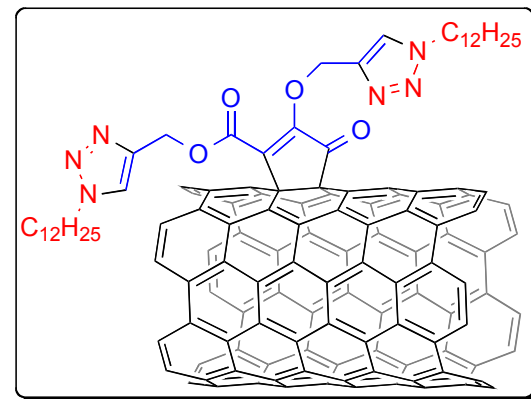
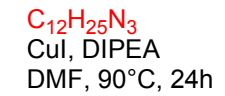
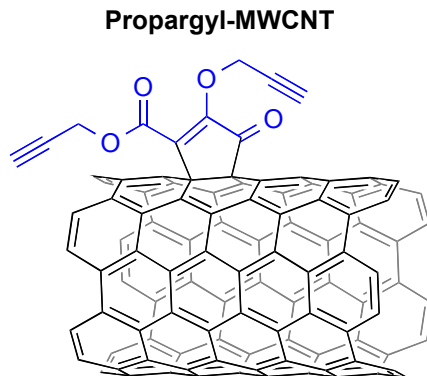
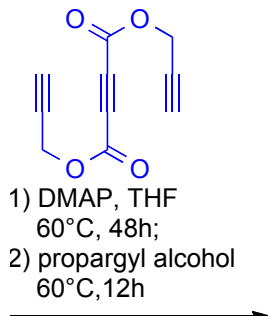
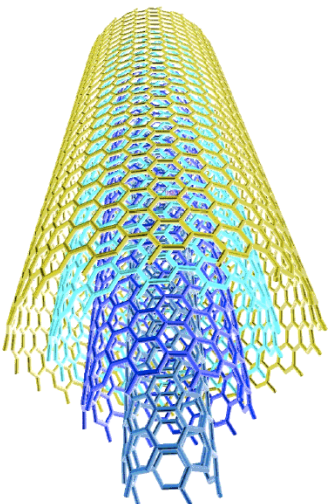
Aliphatic hydrocarbons

Humidity



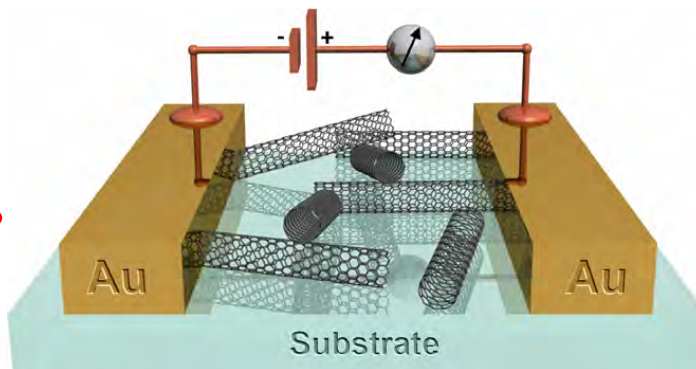
Water

Functionalization of MWCNTs

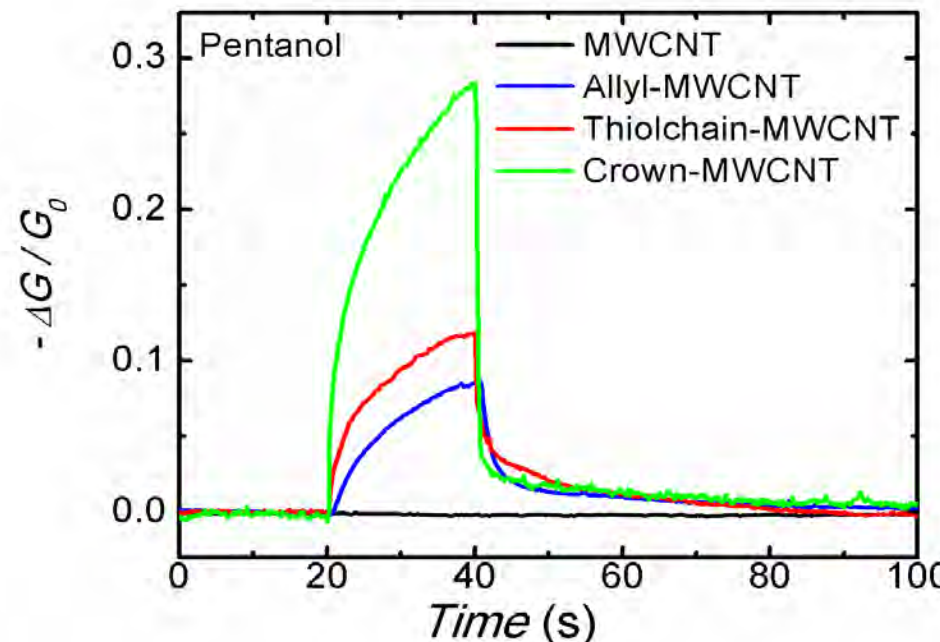
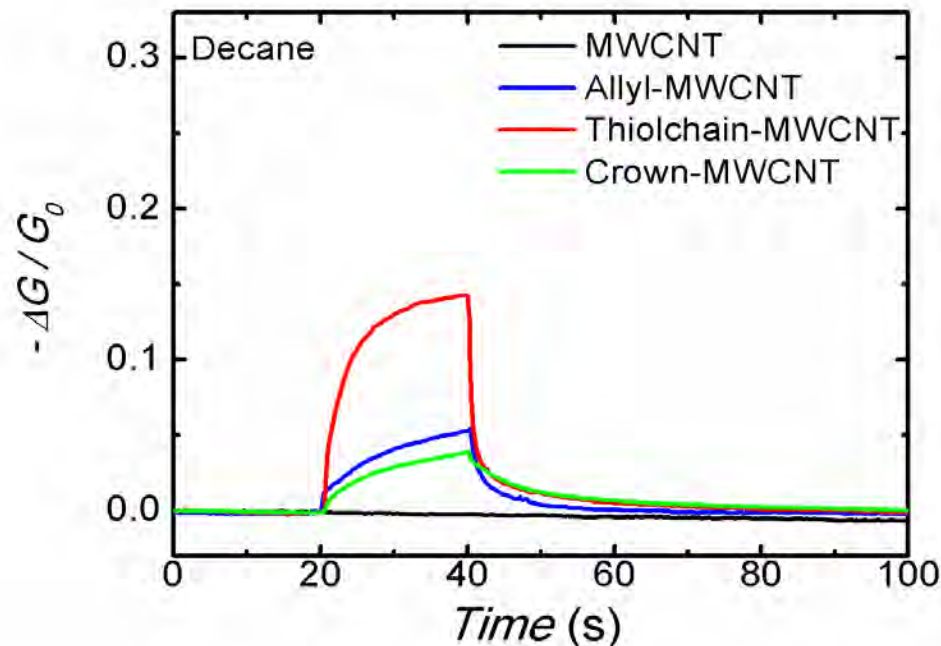


Raw Data From the Sensors

Pristine MWCNTs
Exhibit Small Responses



Reduction in
Conductance
From Increased
CNT Spacing

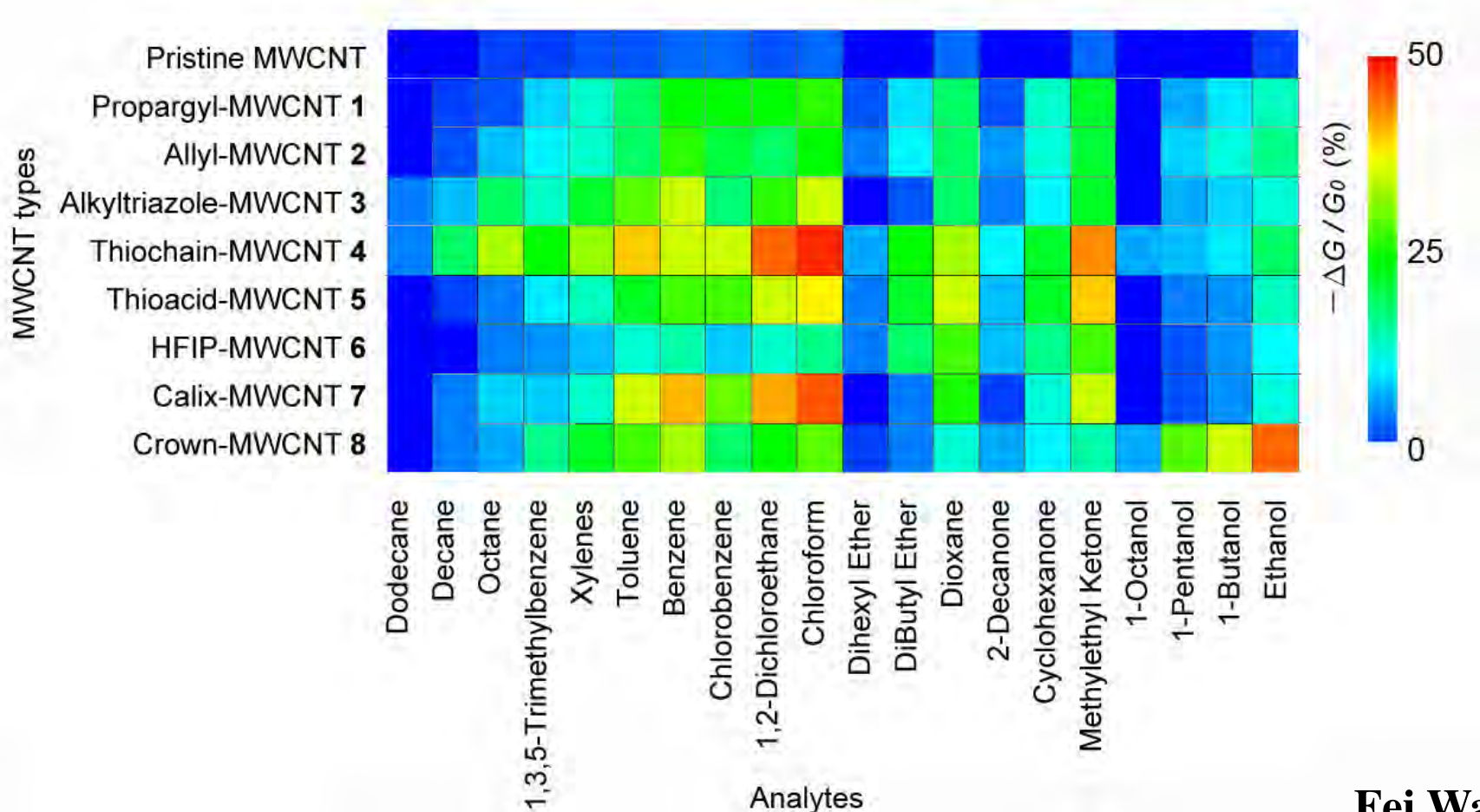


1% of Saturated Vapor
Bias Voltage (0.05 V)

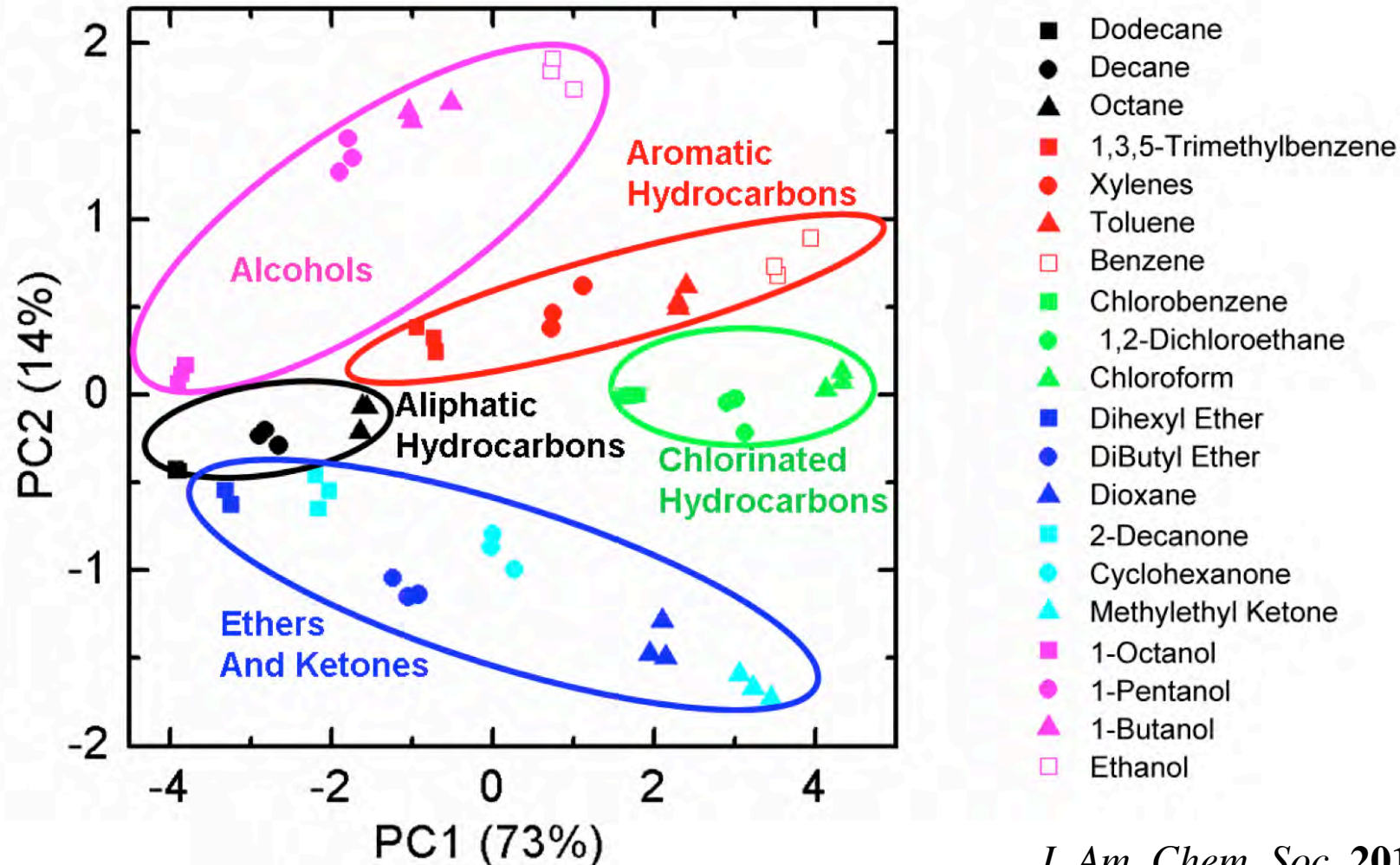
Fei Wang

Response Matrix

- Functionalization Increases Sensing Responses
- Diverse Functional Groups Lead to Cross-Sensitive Responses



Principal Component Analysis

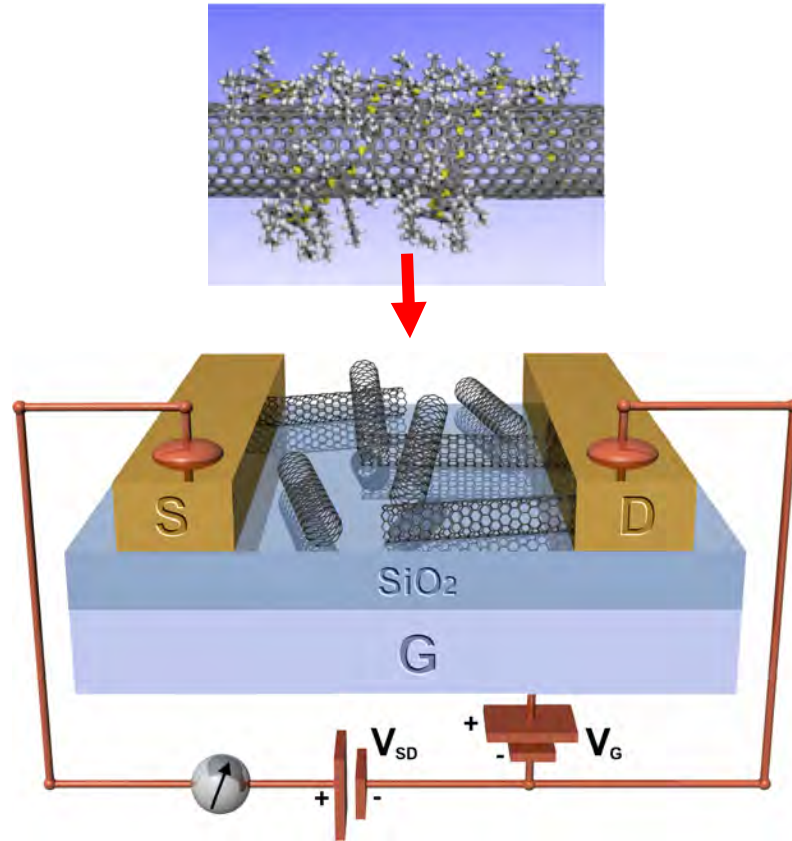


- 23 chemicals are well separated
- 100% Accuracy in Classification with 60 Trials
- Overlaps are result of chemical similarities

J. Am. Chem. Soc. **2011**, *133*,
11181–11193

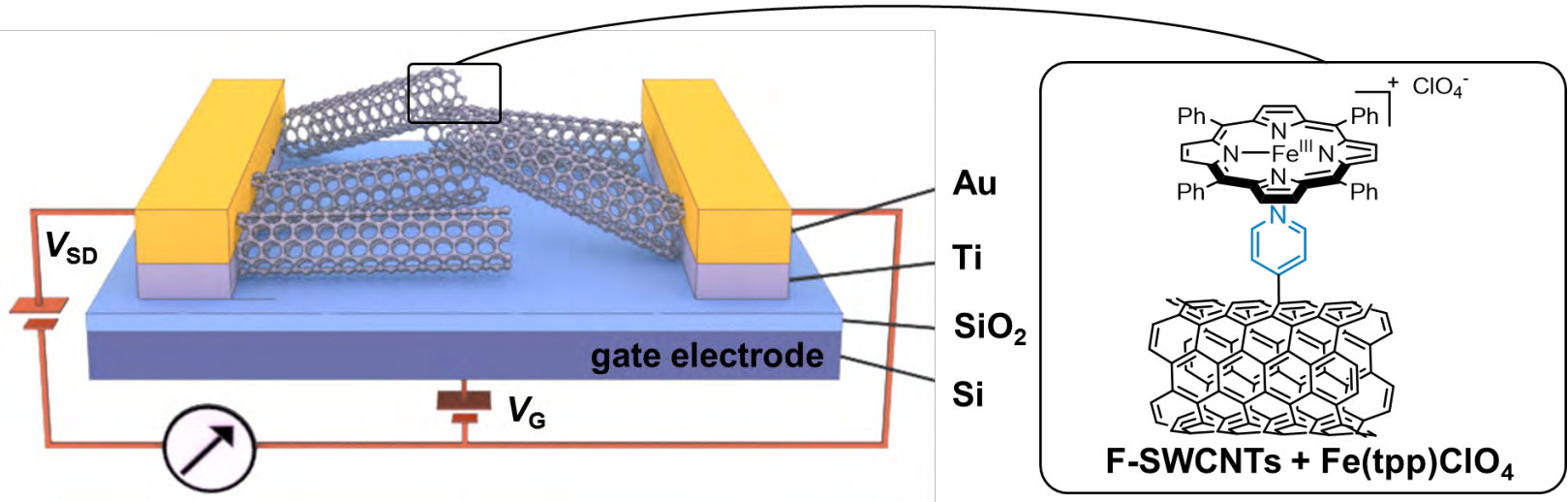
Fei Wang

Gate Voltage Modified Chemiresistors

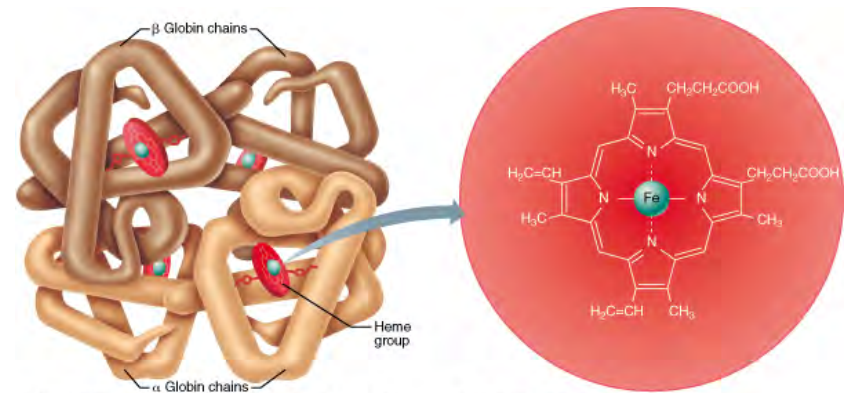


Applying a **Gate Potential (V_G)** Modifies Responses and Adds Dimensionality to Sensor Data

Bioinspired Gate Enhanced Sensors



- Gas sensors modulated by gate voltage
- Bioinspired Materials: harvesting the CO-iron porphyrin interaction



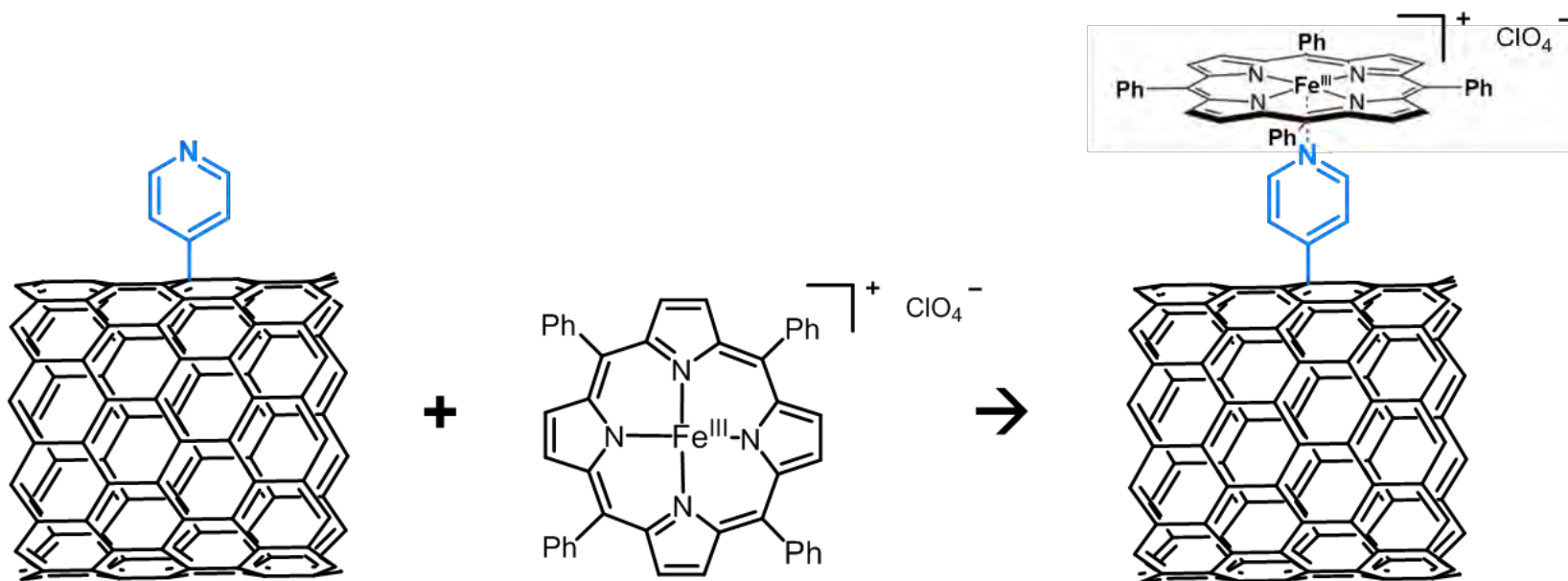
Hemoglobin

Heme group

“All About The Hemoglobin” By Shawn Koshy

Hypotheses

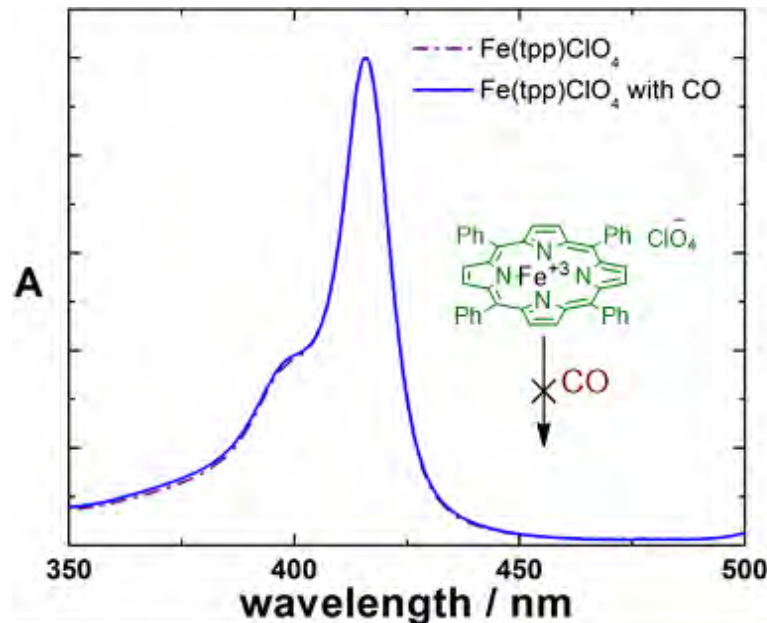
- The pyridine-functionalized CNTs will transduce the binding event
- Application of V_g will reduce the iron porphyrin *in situ*
- The reduction of Fe^{3+} to Fe^{2+} will enhance CO detection



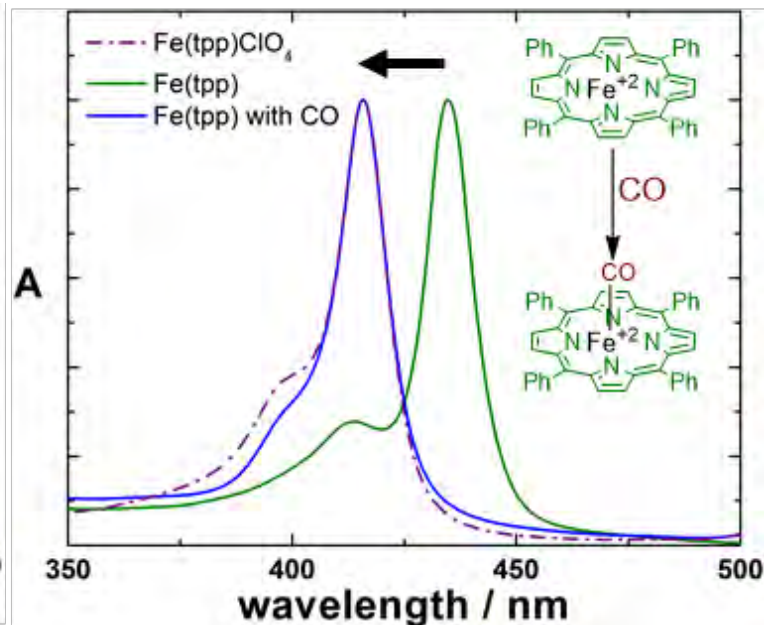
He, M.; Swager, T. M. "Covalent Functionalization of Carbon Nanomaterials with Iodonium Salts" *Chem. Mater.* **2016**, 28, 8542-8549.

Interactions between CO and Fe(tpp)ClO₄

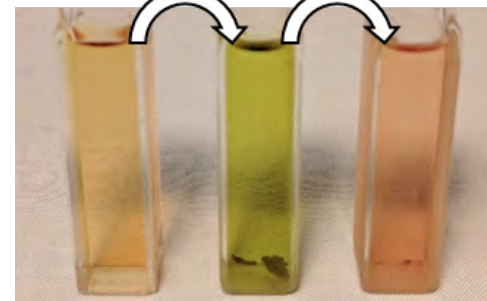
Oxidized Porphyrin



Reduced Porphyrin

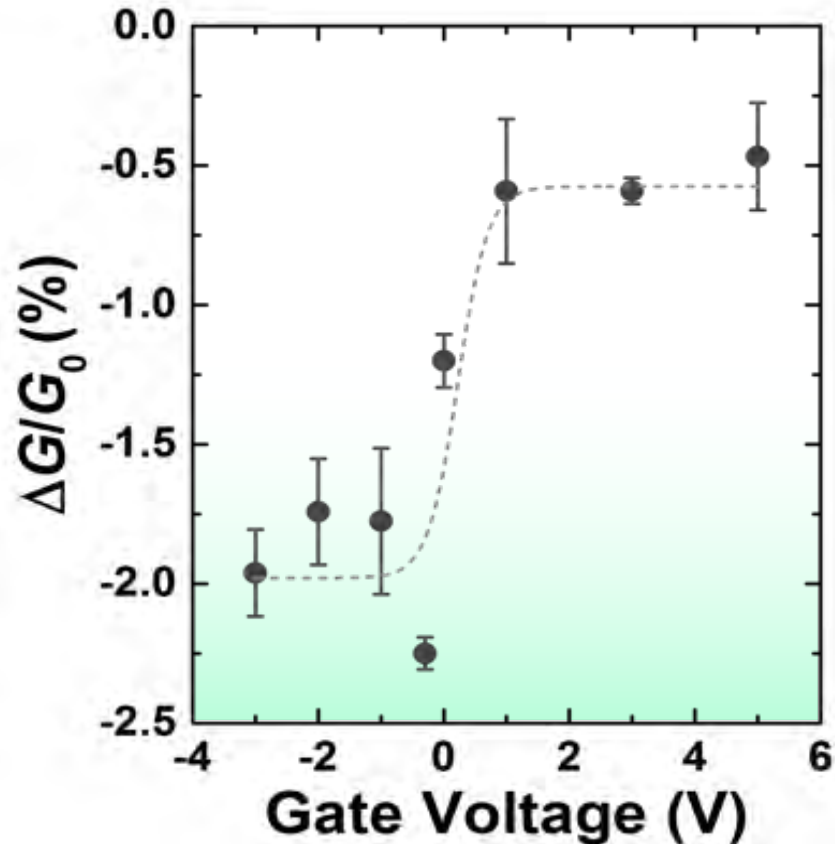
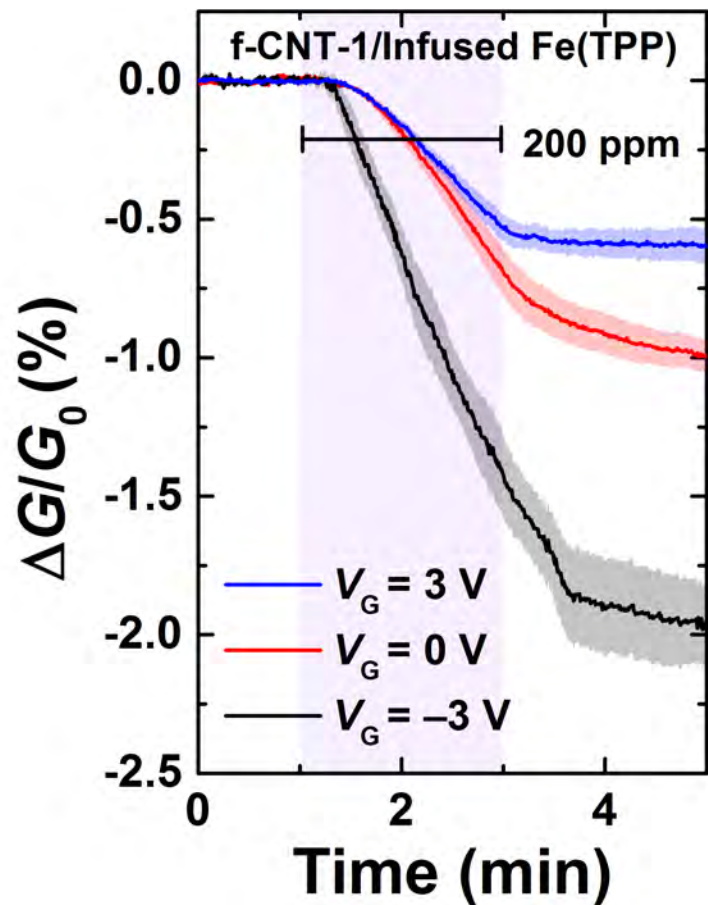


+Na +CO



- Strong response from reduced porphyrin upon exposure to CO
- No response measurable in the UV-Vis of the oxidized porphyrin upon exposure to CO

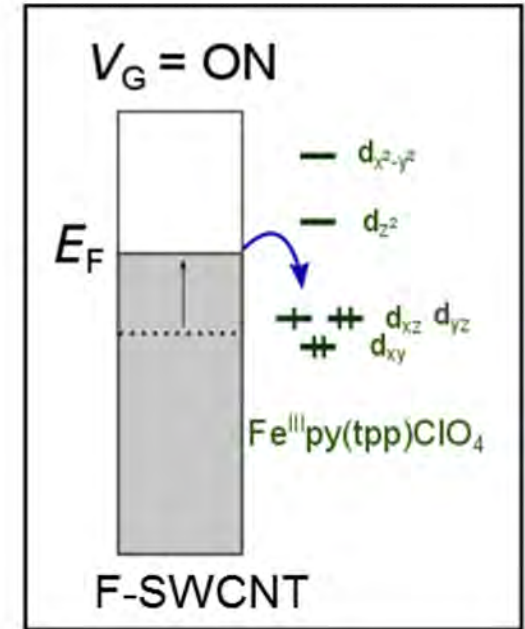
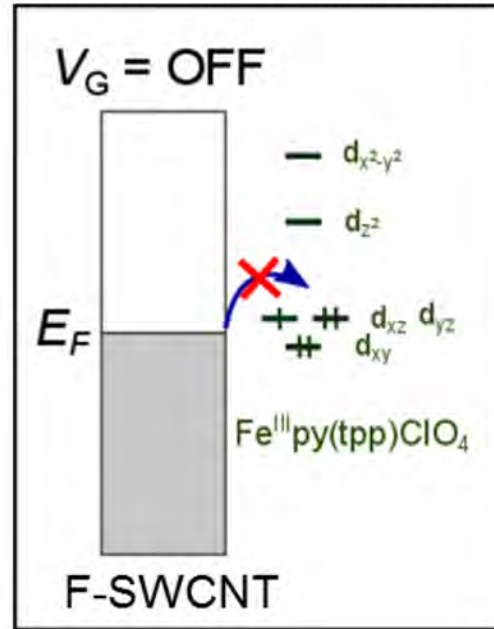
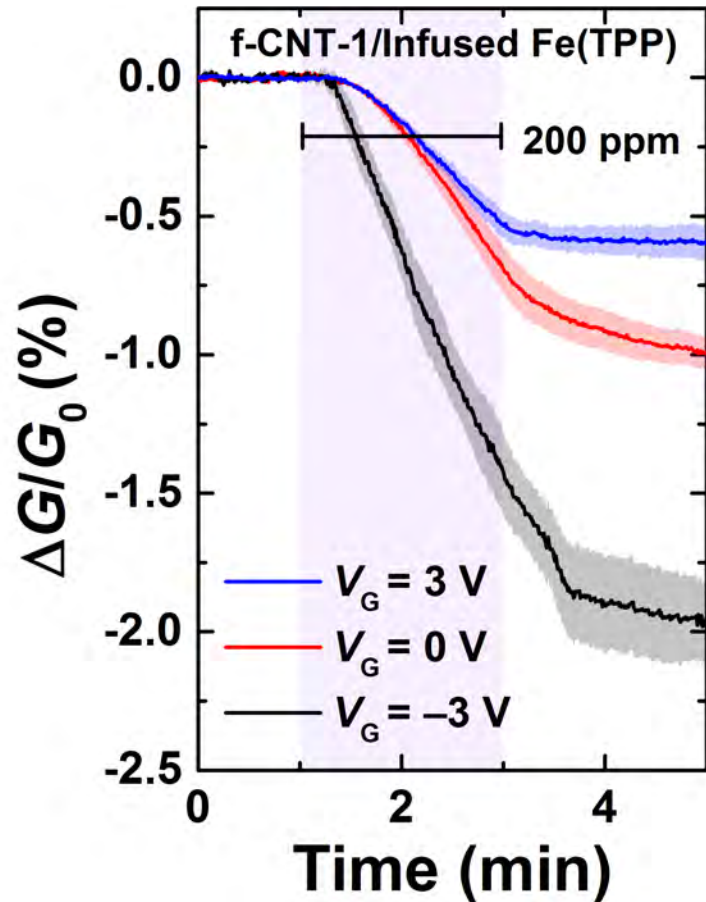
Gate Voltage (V_G) Enhanced Sensitivity



$V_{DS} = 100$ mV, 0.5 L min^{-1} N_2

Savagatrup, S.; Schroeder, V.; He, X.; Lin, S.; He, M.; Yassine, O.; Salama, K. N.; Zhang, X.; Swager, T. M. *Angew. Chem.* **2017**, *56*, 14066-14070

Gate Voltage Enhanced Sensitivity



Gate Voltage Increases the Fe^{II}py(tpp)ClO₄

- Significant improvement in sensitivity towards CO for negative gate voltage
- Modulate the response using V_g

Chemiresistor RFID Sensors

Intrinsic Advantages of Chemiresistors

Low Power/Cost

Small Footprint

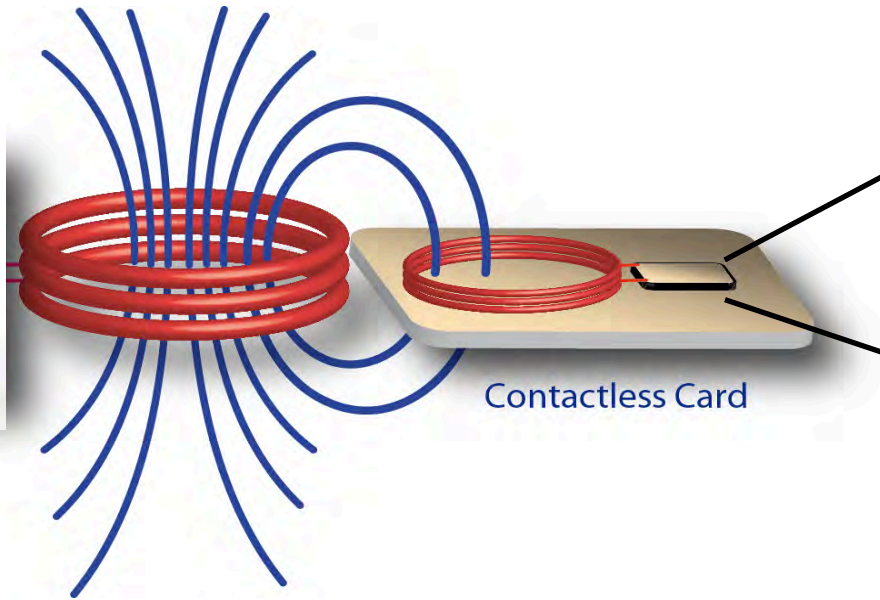
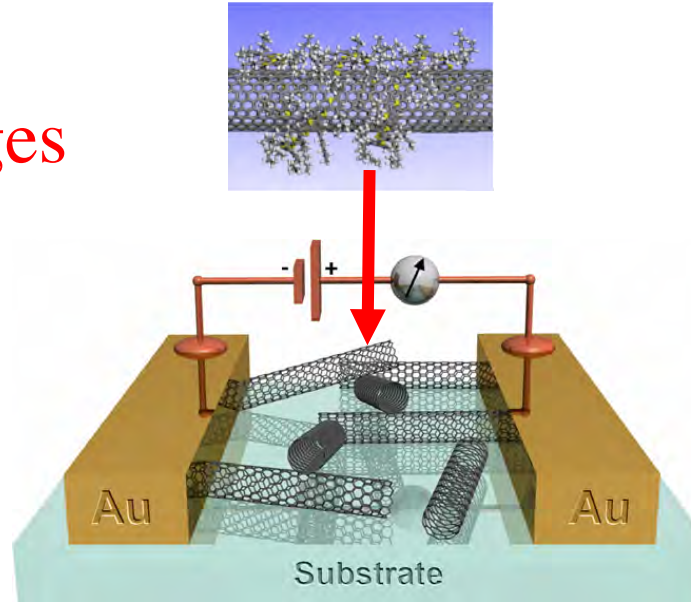
Wireless Network

Technical Needs

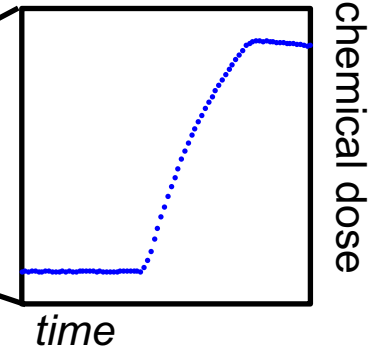
High Sensitivity

Selectivity

No Calibration



Contactless Card



A Sense of Smell for the Digital World



Food

Microphones

Cameras



Home

**Gas Sensors:
Sense of Smell
for the
Digital World**



Industry



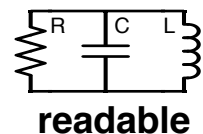
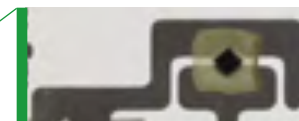
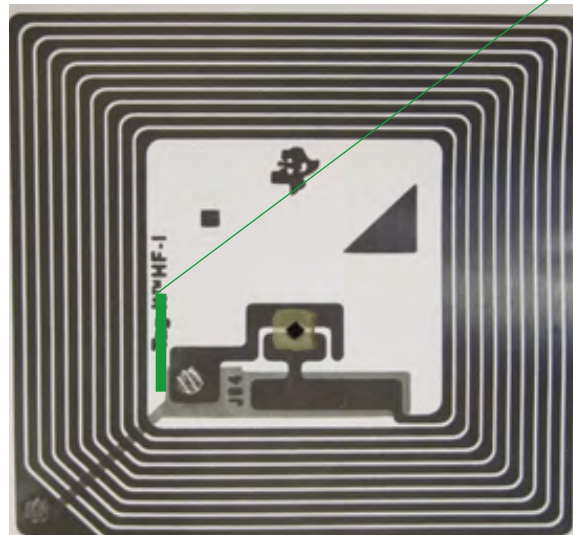
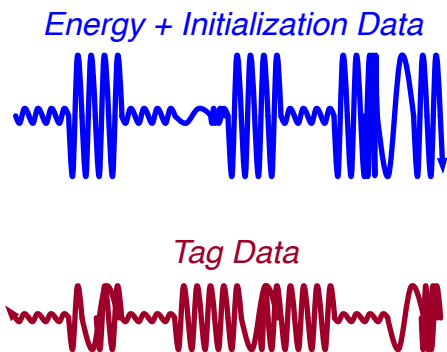
Environment

Physical Sensors

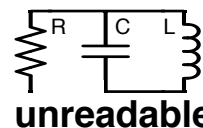
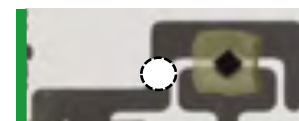


*Smart Phone Apps
Cloud Services
Big Data
Internet of Things*

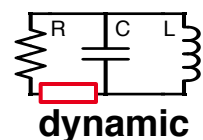
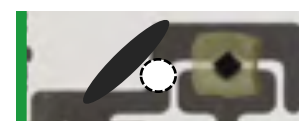
Smartphone Sensing: Ultra-Low Power Wireless Sensors



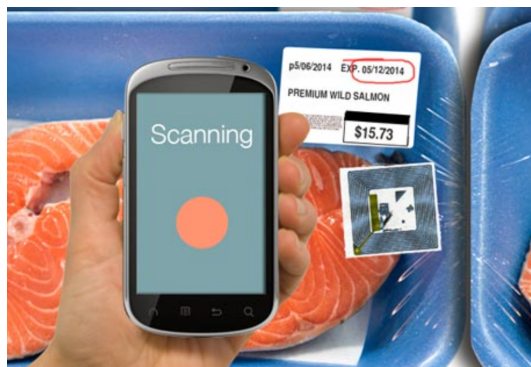
Step 1
↓
Disrupt
Circuit



Step 2
↓
Draw
Sensor



Smart Packaging



**Sensor Tags are
Inductively Powered
and Read by Smartphones**

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{1}{LC} - \left(\frac{R}{L}\right)^2}$$

Azzarelli, J. M., Mirica, K. A., Ravnsbæk, J. B.; Swager, T. M.
Proc. Nat. Acad. Sci. **2014**, *111*, 18162-18166.

Dosimeter Sensors

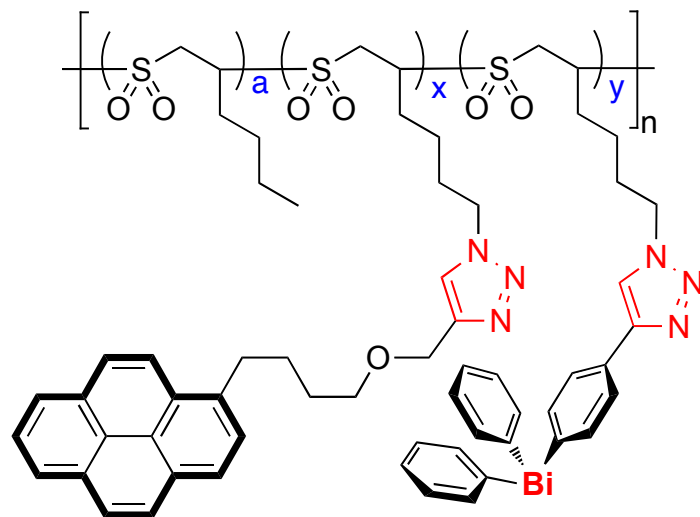
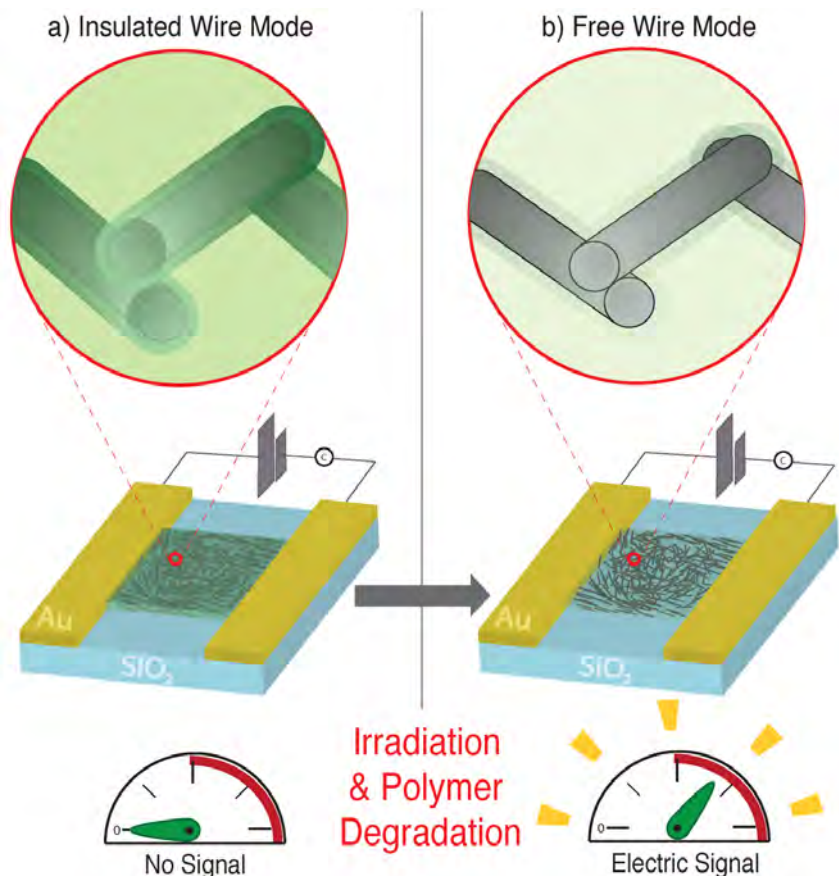
- Dosimeters are Irreversible Sensors
- Provide High Sensitivity ($k_{\text{on}}/k_{\text{off}}$ Vvery Large)
- Cumulative Dosage is Often Most Important
- Ideal for Wearables



γ -Ray Dosimeter by Depolymerization

Large γ -Ray-Crosssection & Meta-Stable Polymer

- Dosimetric Signals can be Preferred
- Higher Sensitivity
- Total Exposures for Environmental Health Monitoring



Jose Lobe, TMS

Angew. Chem. Int. Ed. **2010**, *49*, 95

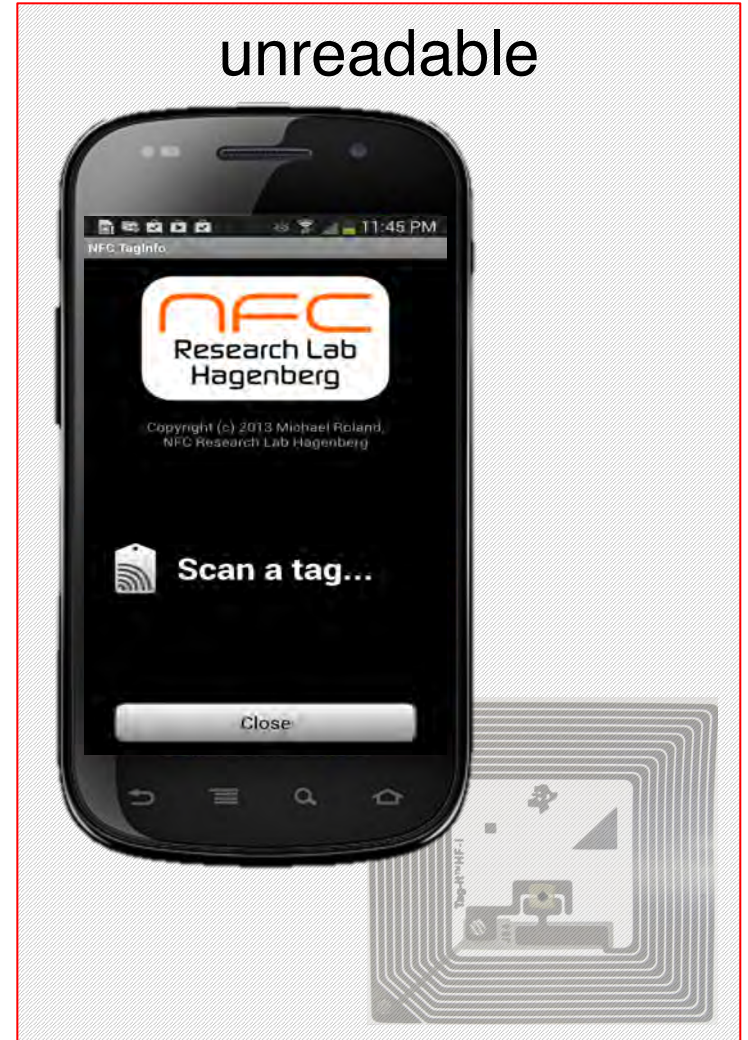
Dosimeter Tags: Readable or Unreadable

readable



or

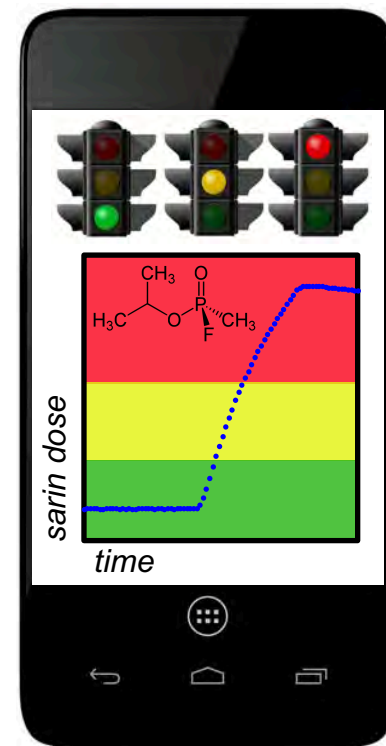
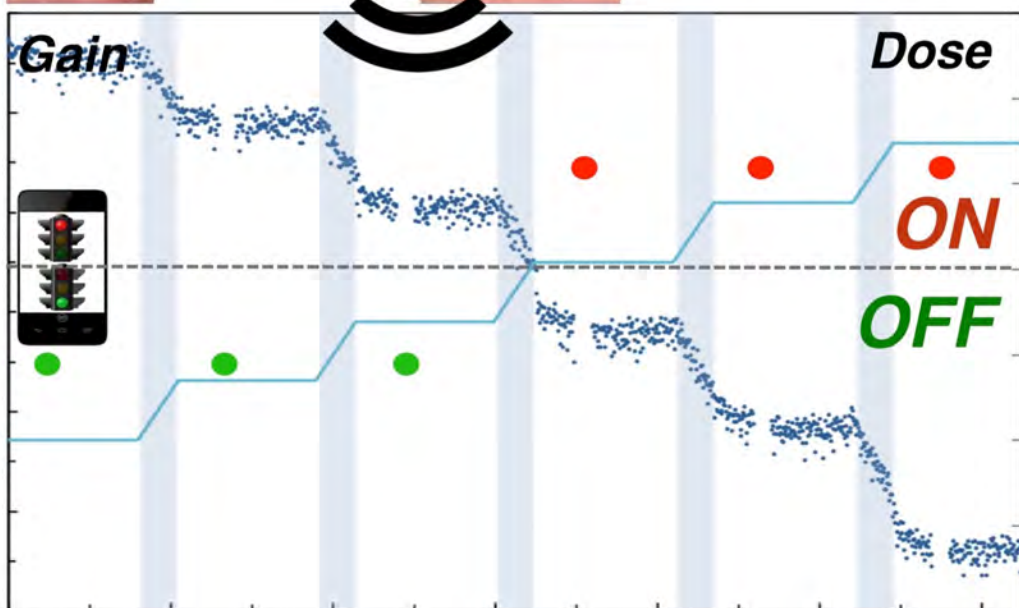
unreadable



Sensor Tags For Explosives Detection

Azzarelli, J. M., Mirica, K. A., Ravnsbæk, J. B.; Swager, T. M. “Wireless Gas Detection with a Smartphone via RF Communication” *Proc. Nat. Acad. Sci.* **2014**, *111*, 18162-18166.

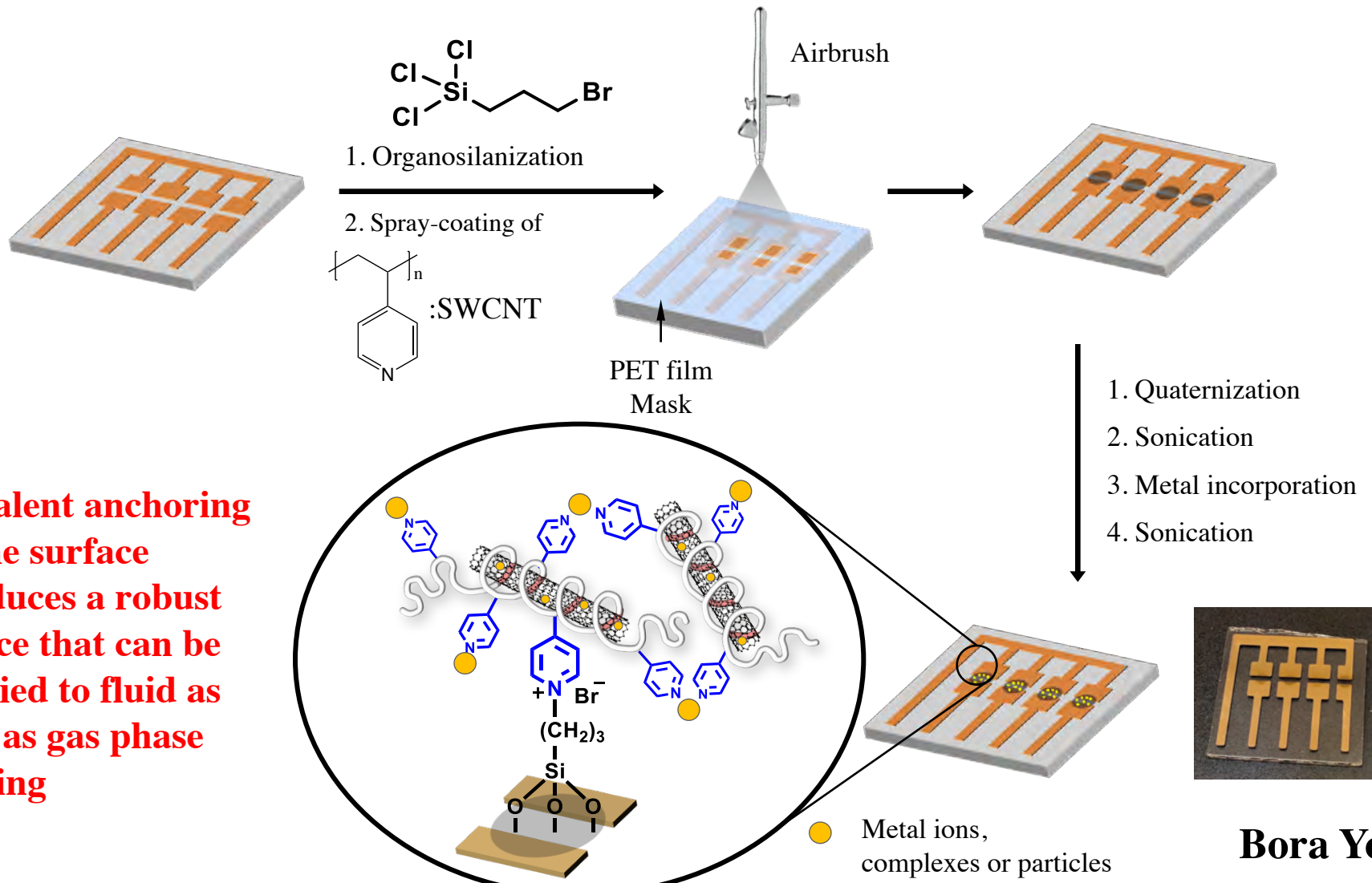
Wearable Chemical Dosimeters



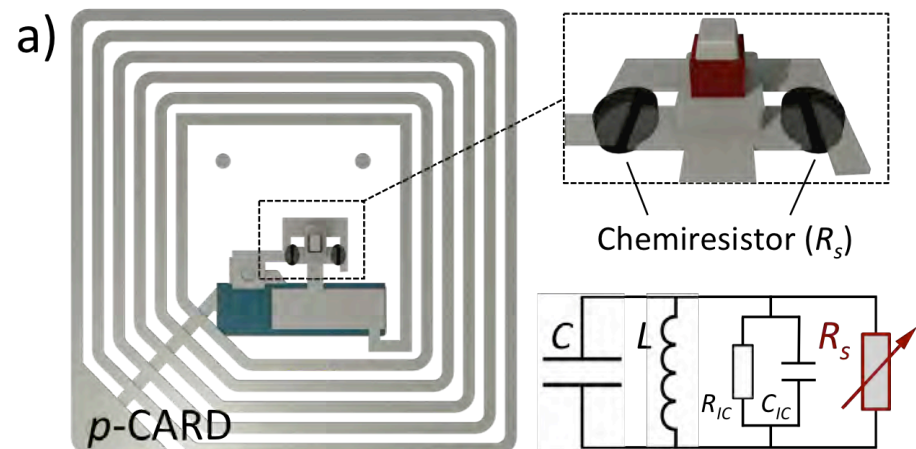
Zhu, R.; Azzarelli, J. M.; Swager, T. M.
Angew. Chem. Int. Ed. **2016**, *55*, 9662.

Ishihara, S.; Azzarelli, J. M.; Swager T. M.
J. Am. Chem. Soc. **2016**, *138*, 8221.

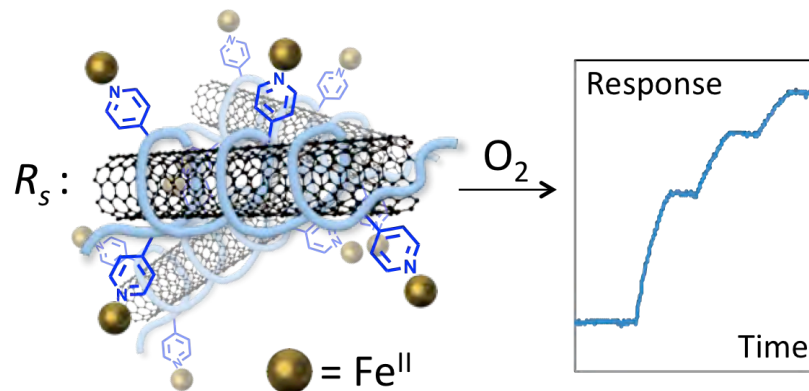
Fabrication of Sensor Devices with Surface Anchored SWCNTs



Food Packaging: Non-Line-of-Sight Detection of Freshness

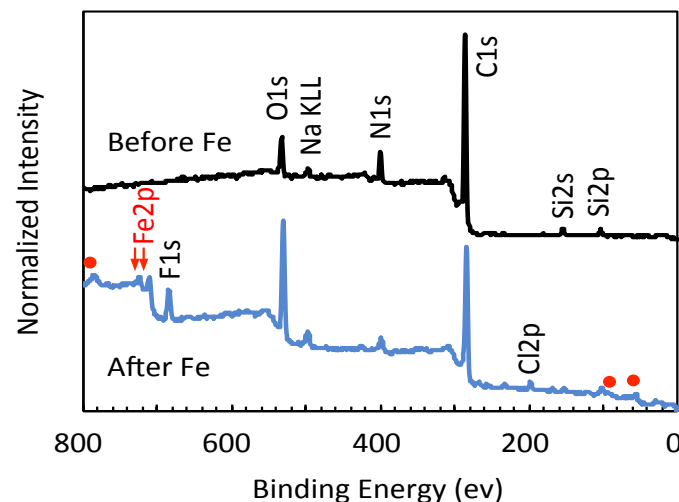
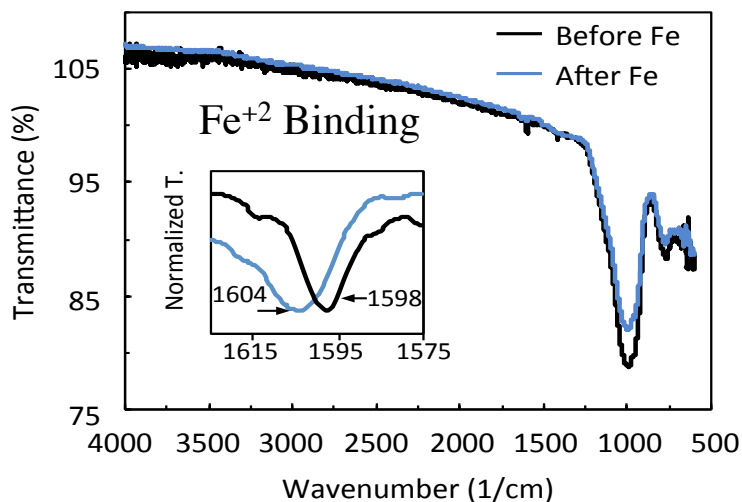
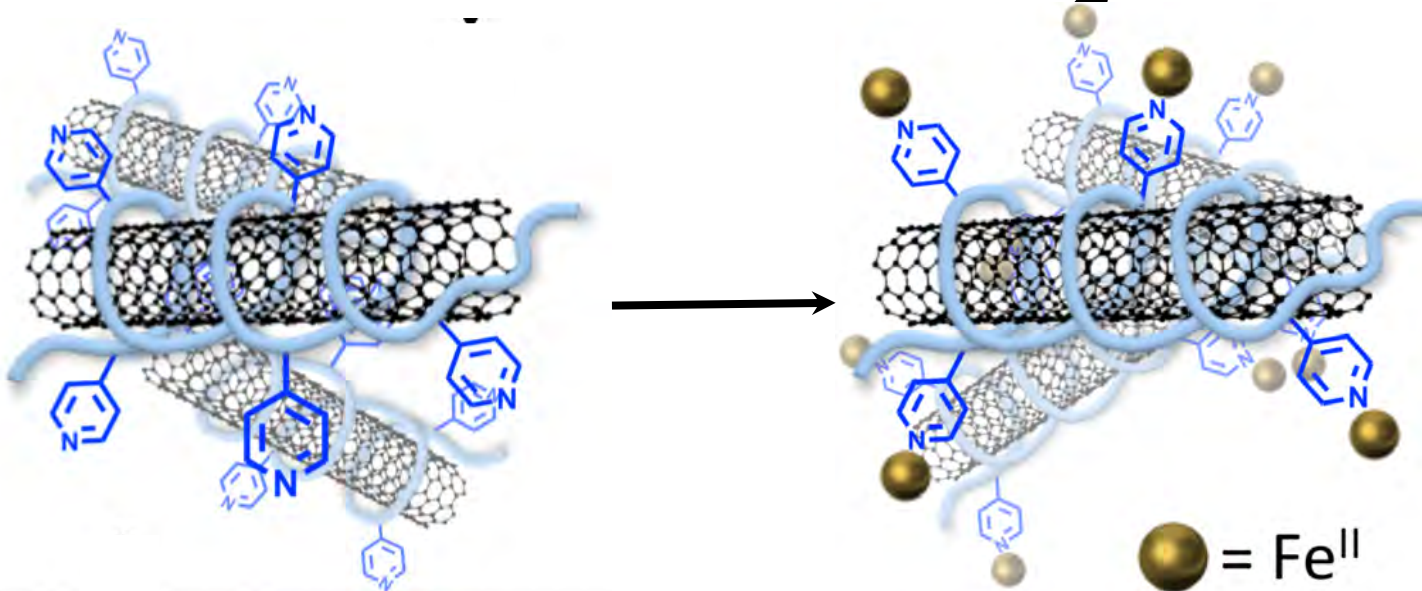


b) O_2 - p -CARD:



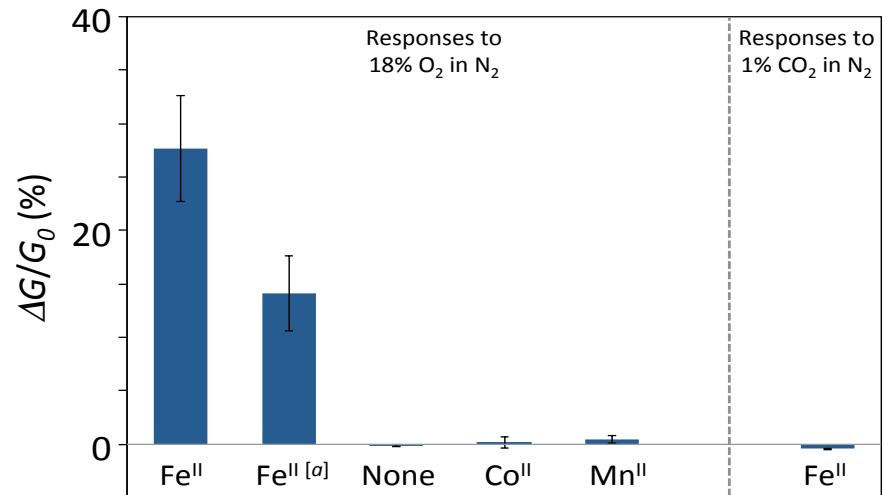
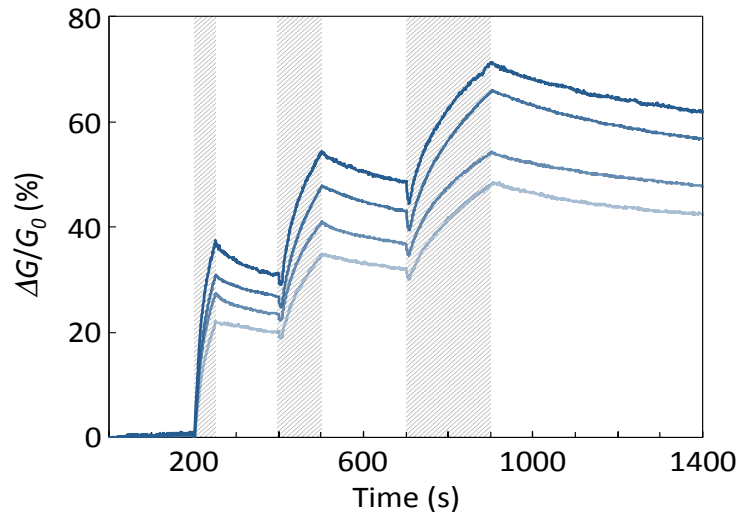
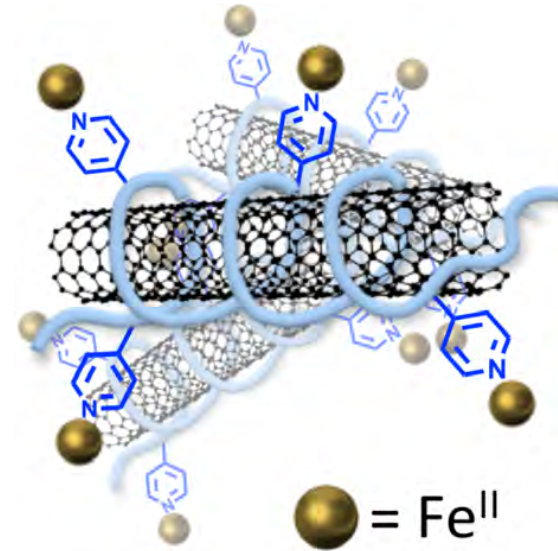
Zhu, R.; Desroches, M.; Yoon, B.; Swager, T. M. "Wireless Oxygen Sensors Enabled by Fe(II)- Polymer Wrapped Carbon Nanotubes" *ACS Sensors*, **2017**, 2, 1044-1050.

Sensor Formation and O₂ Response

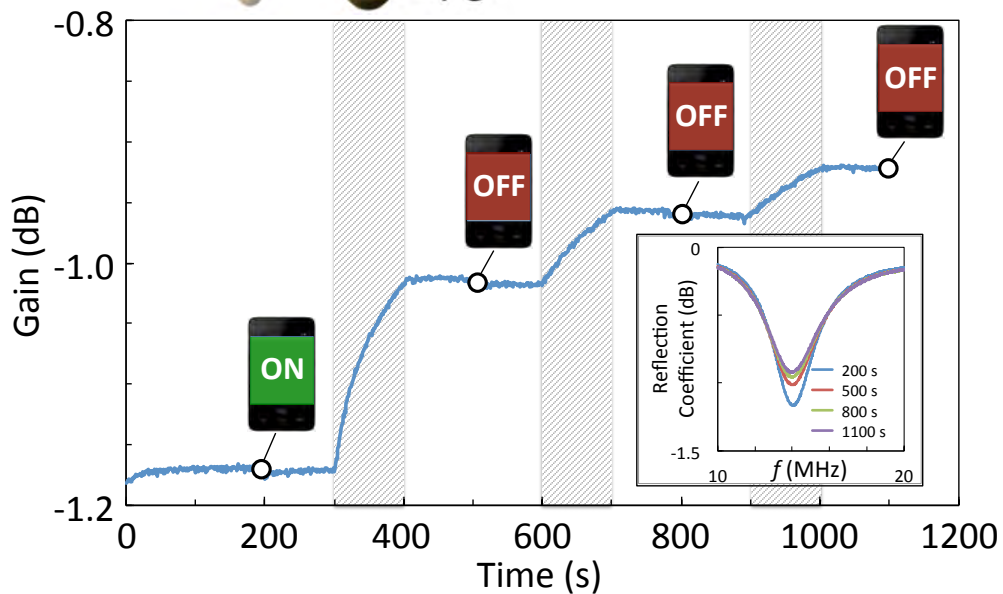
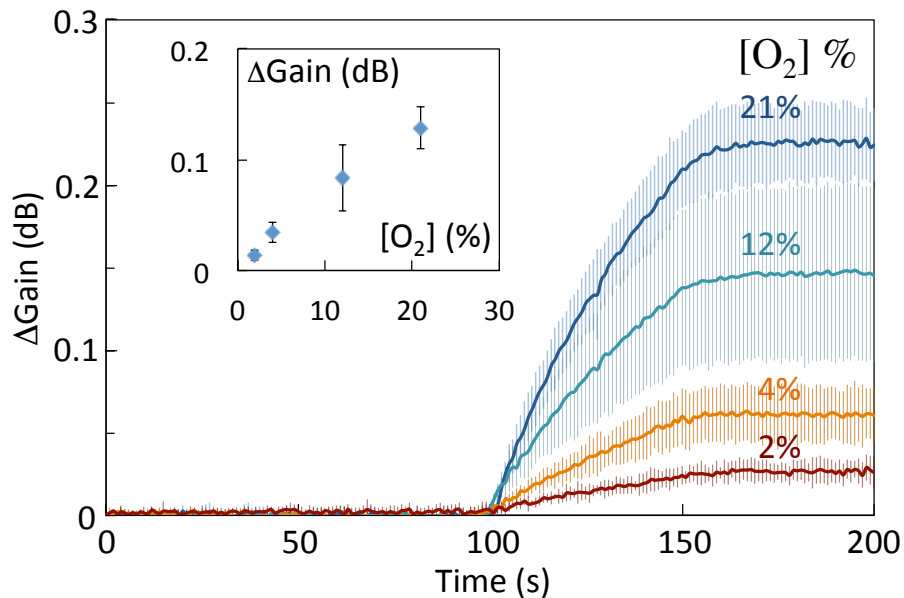
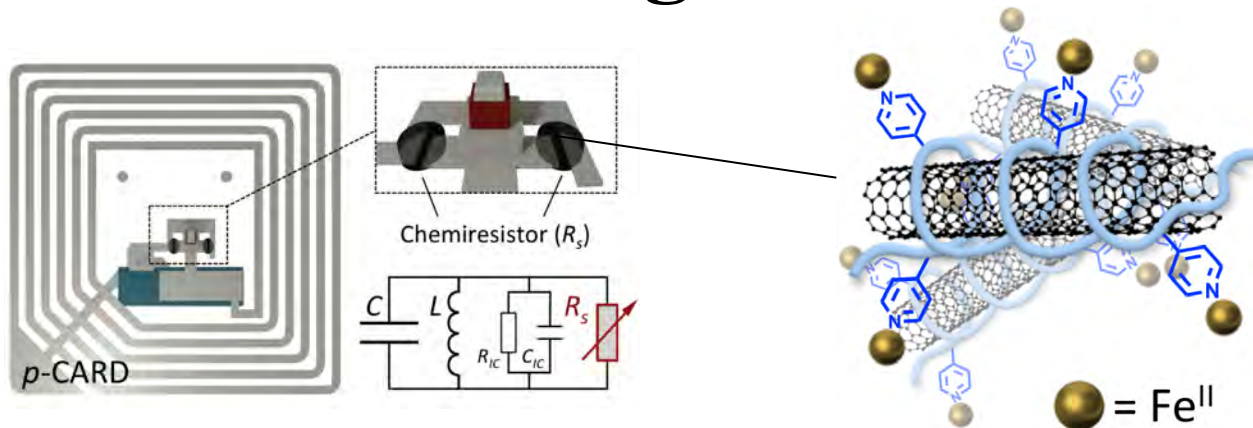


Sensor Formation and O₂ Response

- Response to 18% O₂ in N₂
- Dosimeter Behavior
- No CO₂ Response
- Co^{II} and Mn^{II} are Ineffective



Passive RFID Tag Sensors and Smart Phone Digital Readout



Rong Zhu



Only Possible With Great Co-Workers