

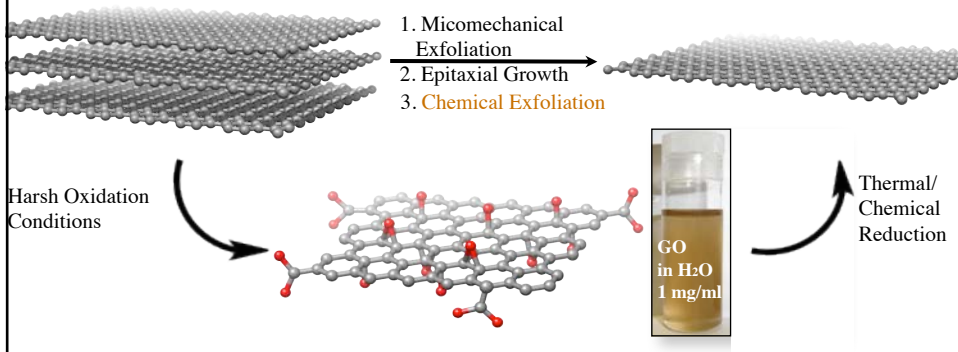
Chemistry of the Graphene Surface for the Creation of Functional Nanomaterials

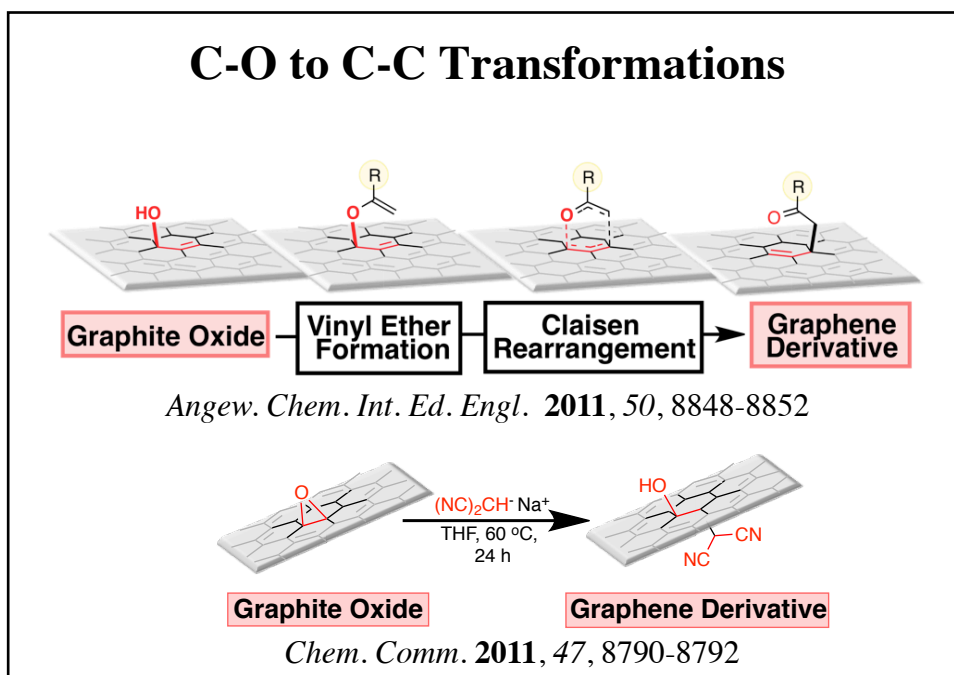
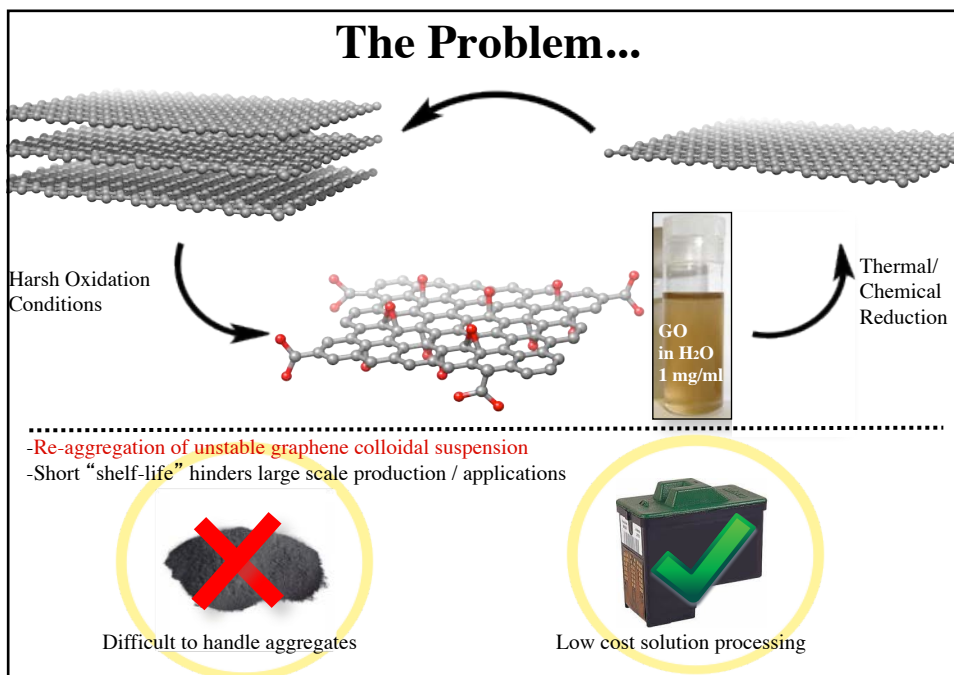


MIT ILP NanoTech Conf.
Timothy M. Swager

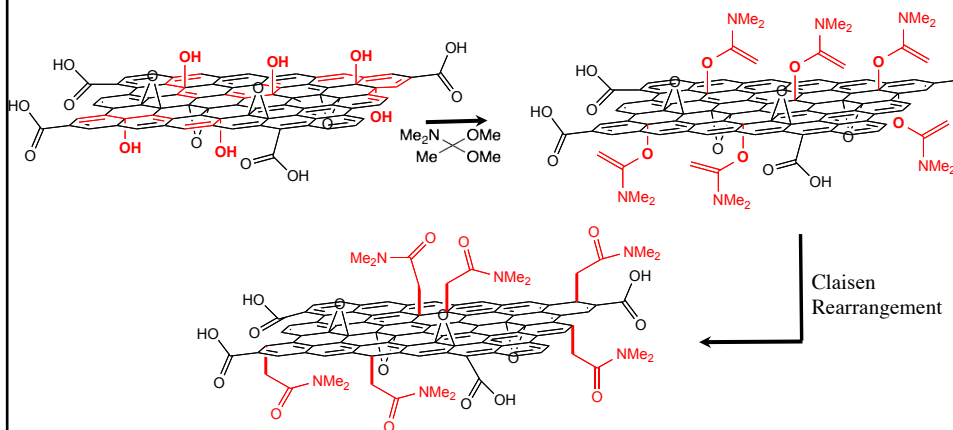


How Do You Make/Use Graphene?

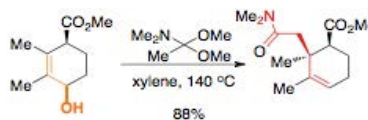




Transformations of Graphite Oxide

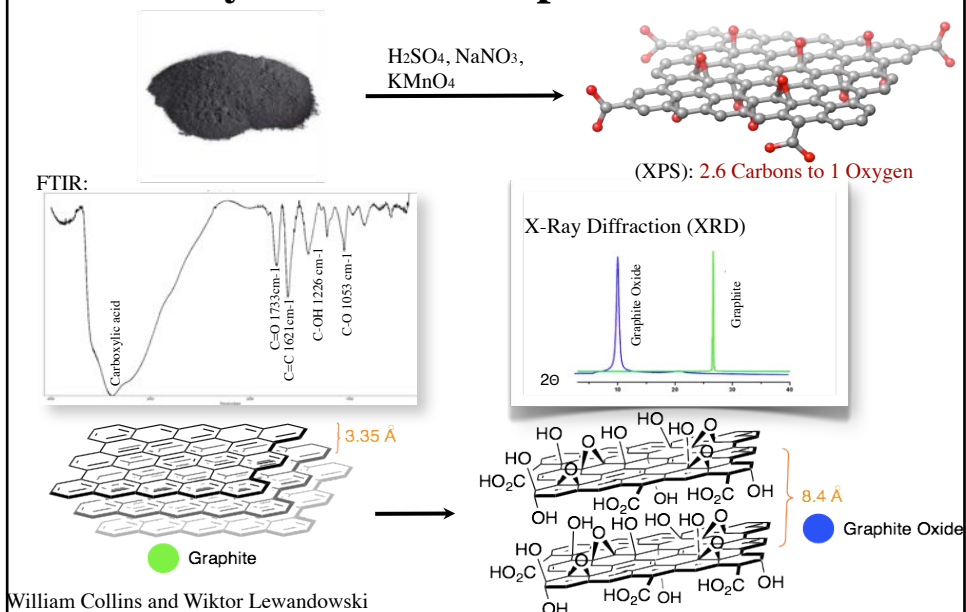


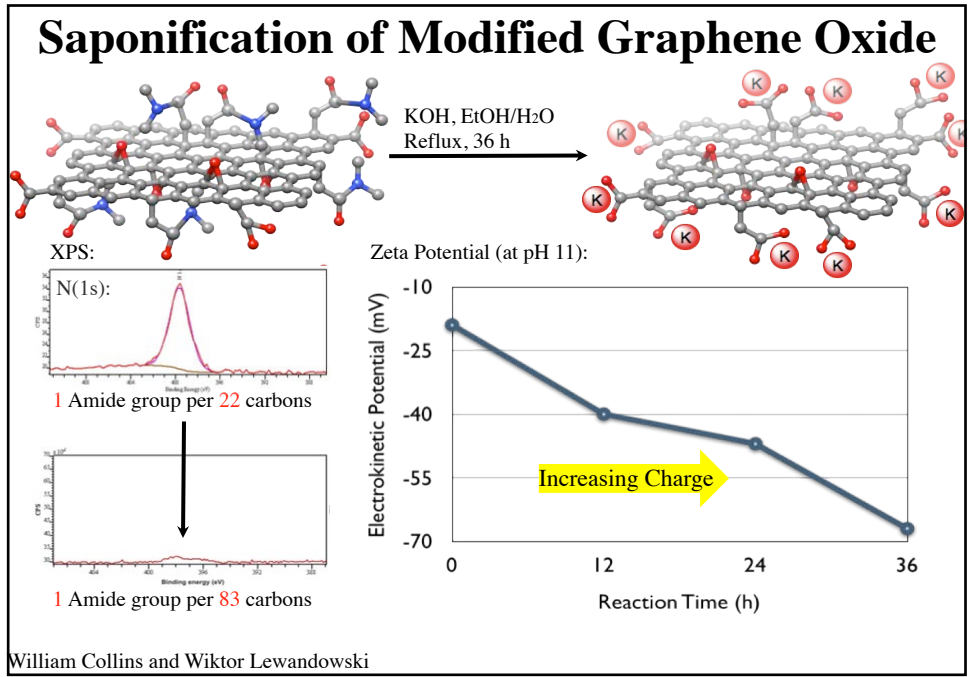
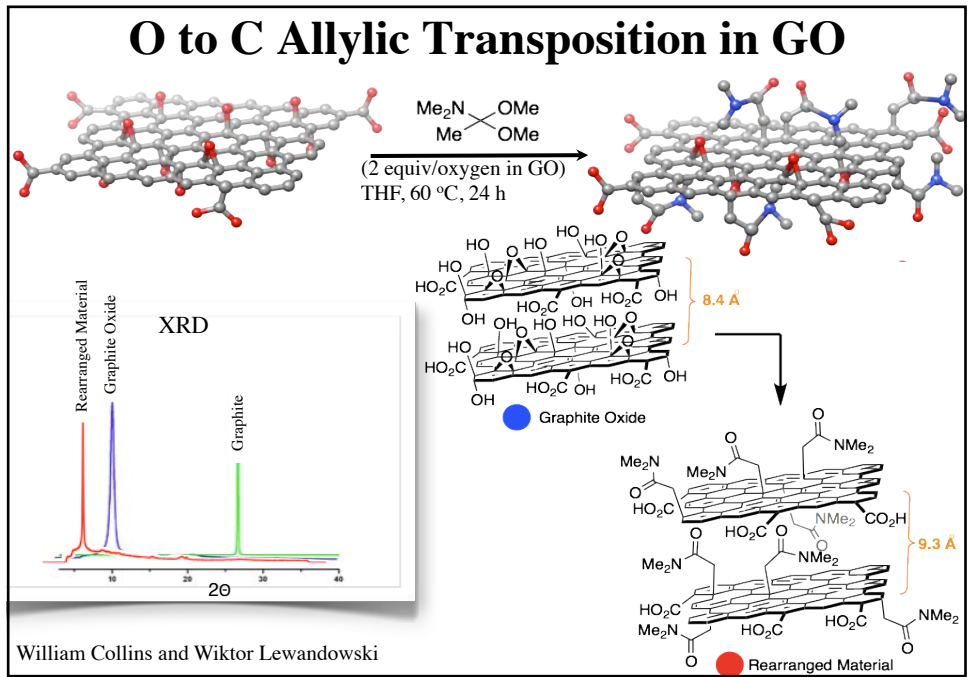
N,N-dimethylacetamide dimethylacetal **only** reacts with the alcohols **Nitrogen (N 1s)** incorporation can be quantified

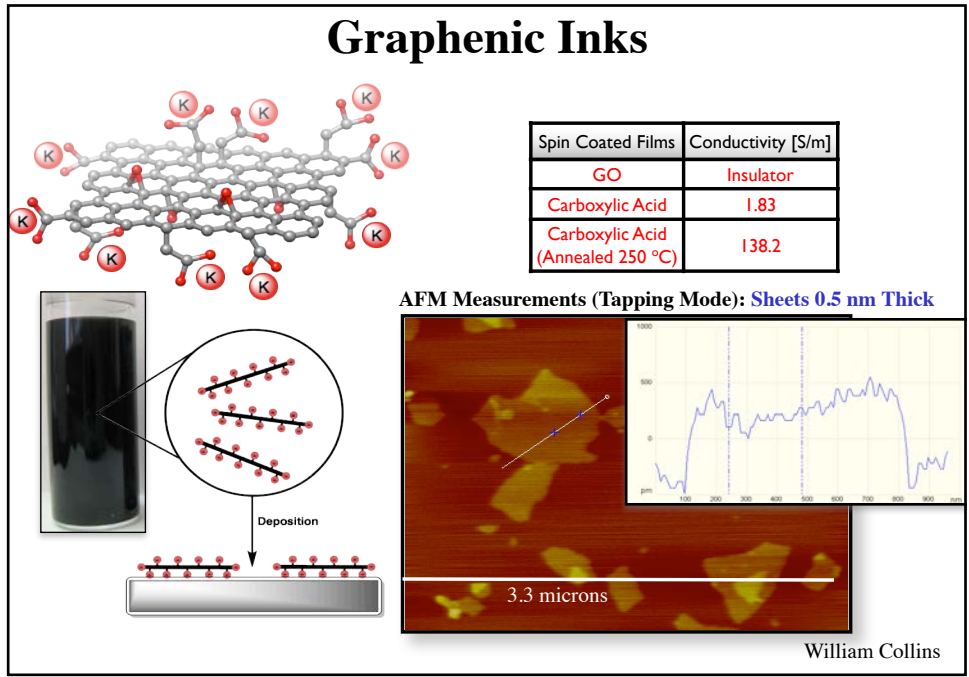
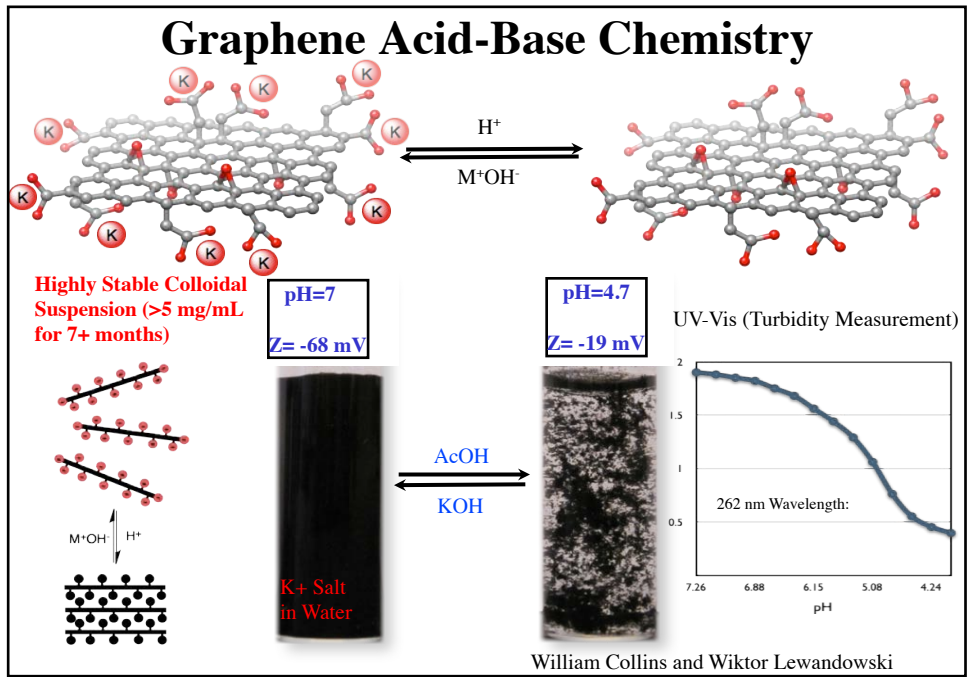


Eschenmoser, A. *et. al. Helv. Chem. Acta.* (1969), **52**, 1030.

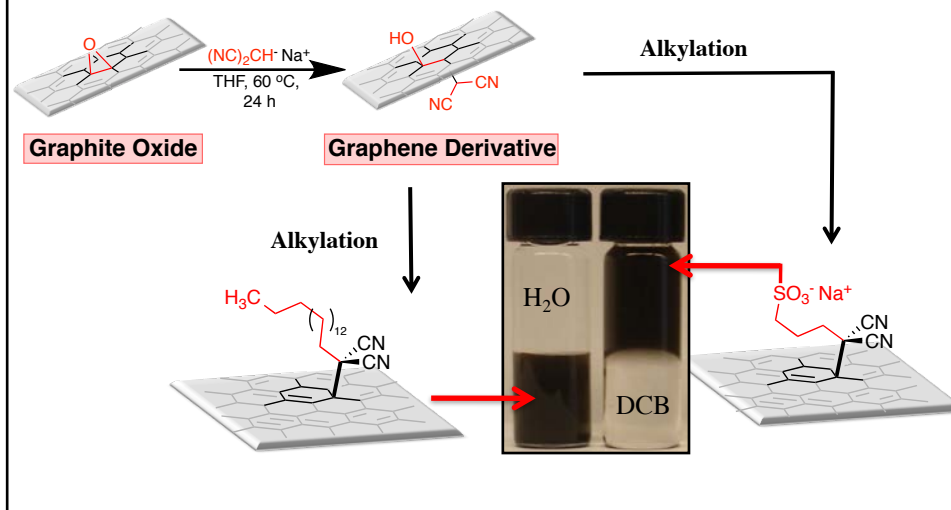
Synthesis of Graphite Oxide





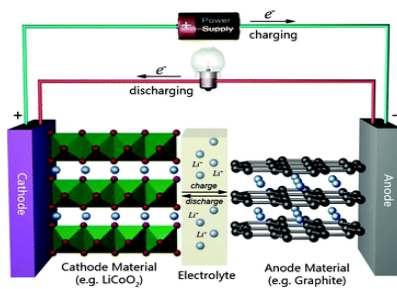


Reactions of GO with Less Reducing Carbanions



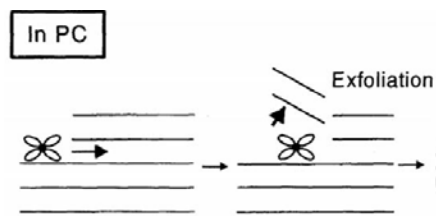
Electrochemical Graphene Exfoliation

Functional Graphene w/o Added Oxygen Defects



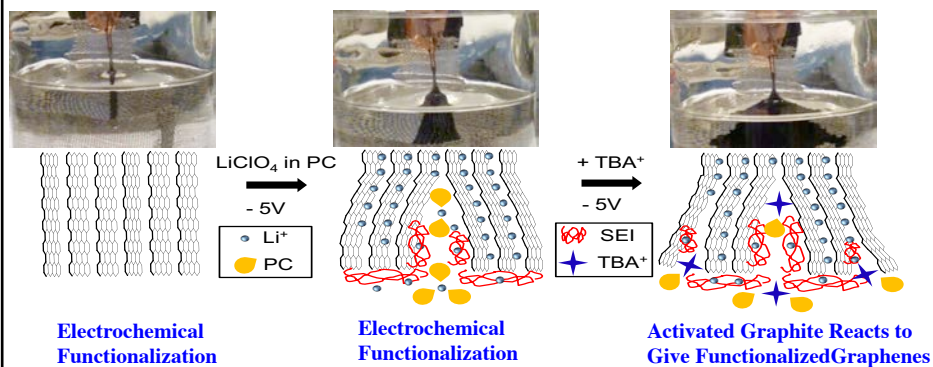
Solvent Molecules
Co-intercalate with Li^+
Graphite Intercalated
Compounds
(GIC, $\text{Li}_x(\text{solv})_y\text{C}_n$)

Li ion Batteries can Rupture and Exfoliate in Propylene Carbonate Electrolyte System



Ogumi et al., Bull. Chem. Soc. Jpn 71, 1998

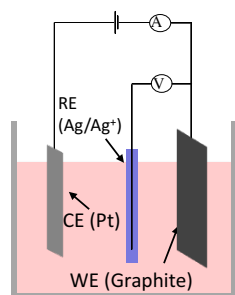
Electrochemical Exfoliation/Expansion of Graphite



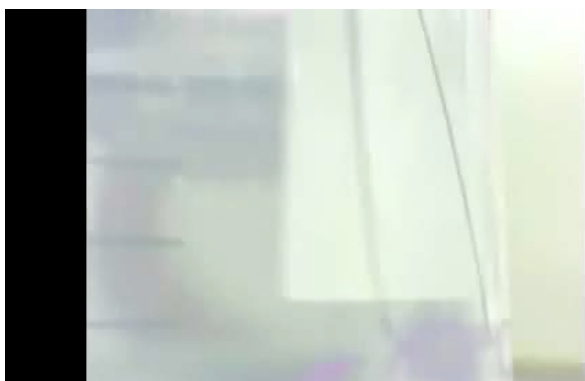
Zhong, Y. L.; Swager, T. M. "Enhanced Electrochemical Expansion of Graphite"
J. Am. Chem. Soc. **2012**, *134*, 17896-17899.

Electrochemical Activation of HOPG

Electrochemical Set-Up

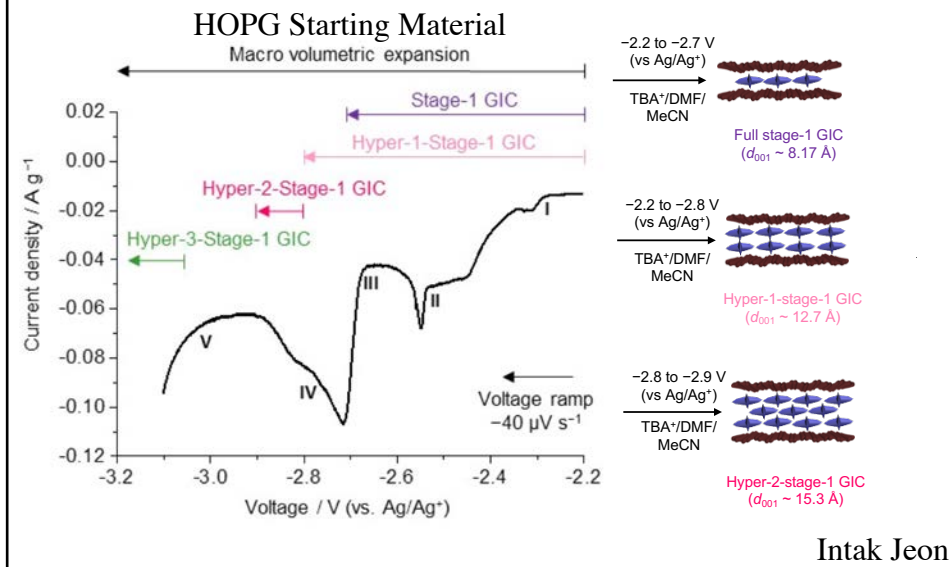


Electrolyte
(TBA⁺/ACN/DMF)

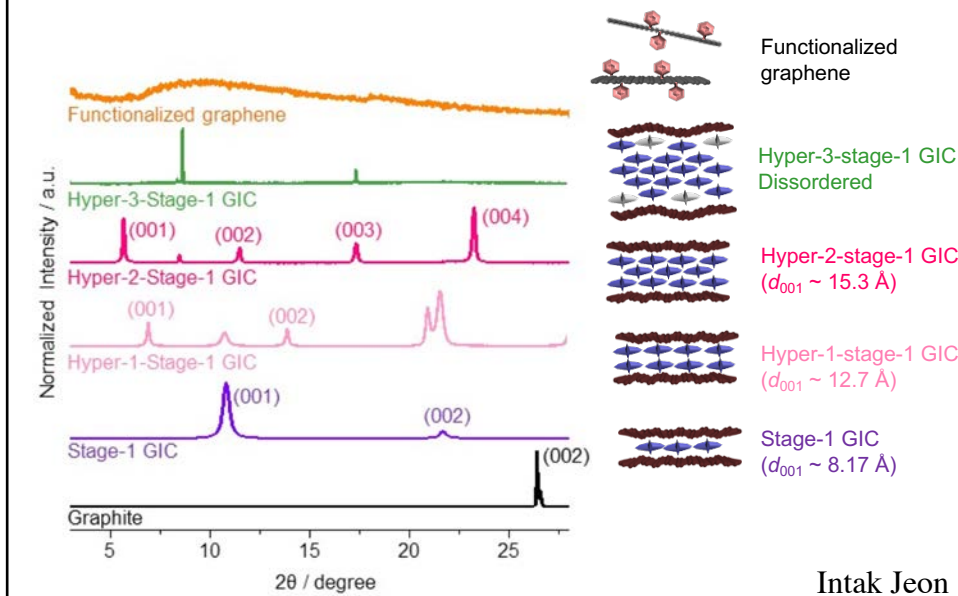


Final potential -2.22V vs
Ag/Ag⁺

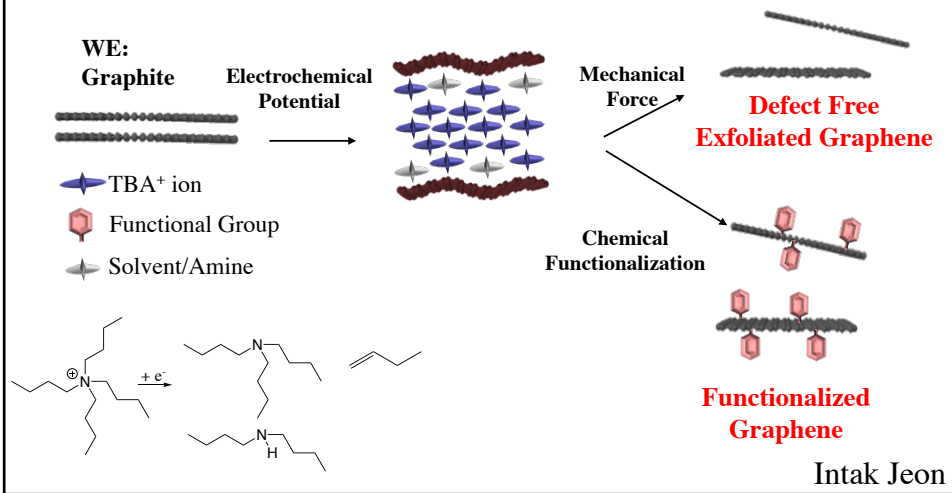
Staged Electrochemical Graphene Synthesis



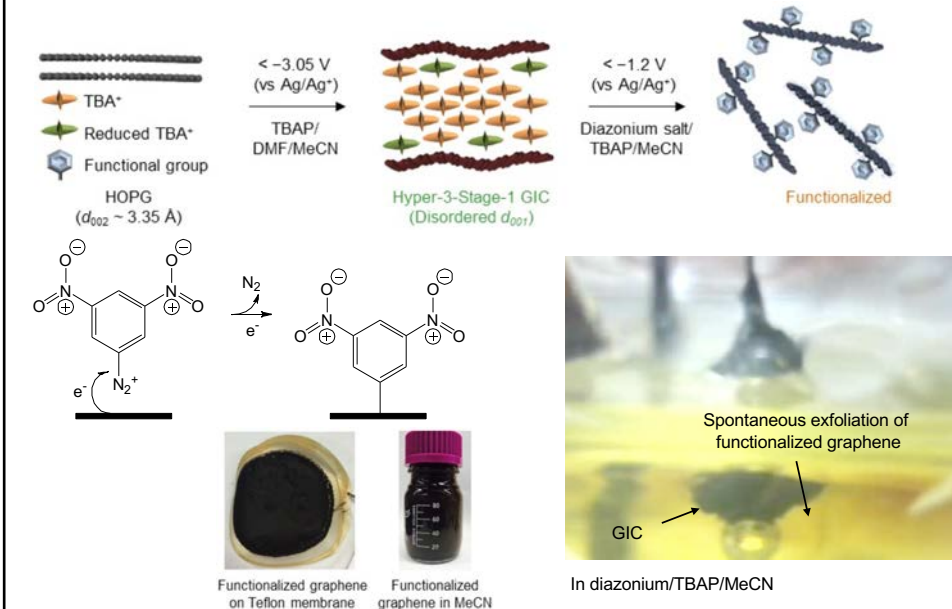
XRD of Graphene Intercalation Compounds



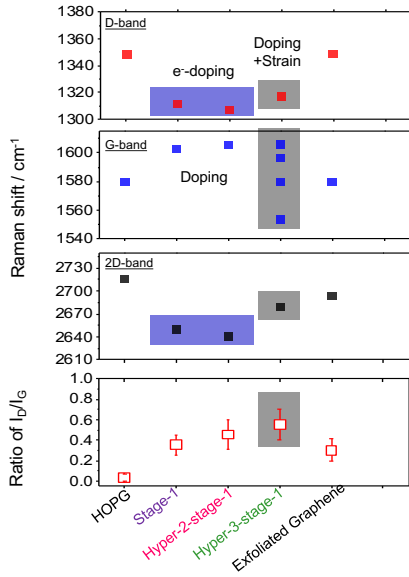
Utility of the Hyper-3-stage-1 Graphite Intercalation Compound



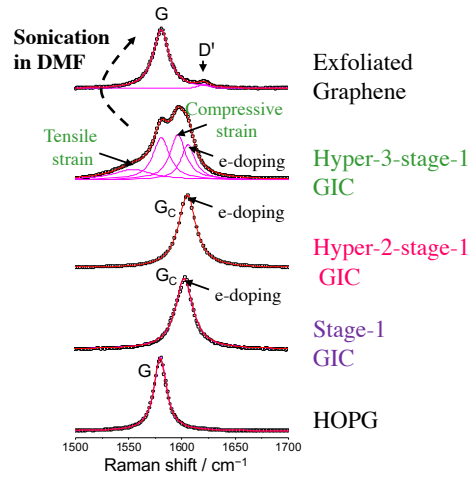
Spontaneous Reactive Exfoliation



Raman Characterization

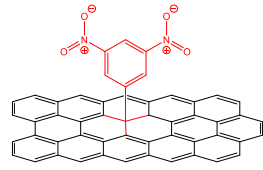


A. Das, A. Ferrari et al., Nat. Nanotecnol. 3, (2008) 210
 A. Ferrari et al., Nat. Nano Nanotecnol 8, (2013) 235
 O. Frank, C. Galotis et al., ACS Nano, 4 (2010) 3131



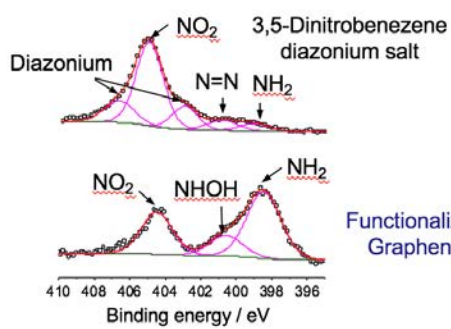
Intak Jeon

Graphene Functionalization

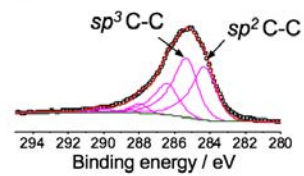


N/C Ratio and XPS:
 A Pendant Ar for Every 2 Graphene Rings!
 Reduction of the NO₂ Groups
Raman:
 Very Broad with D/G = 0.7

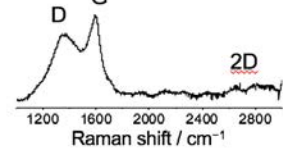
XPS N1s



XPS C1s



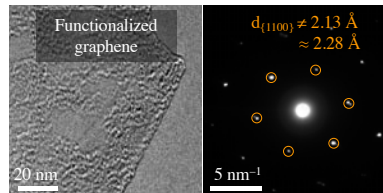
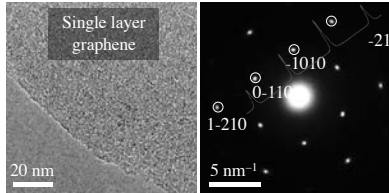
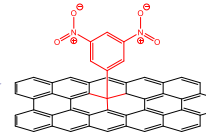
Raman



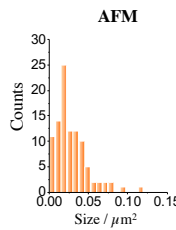
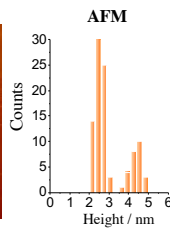
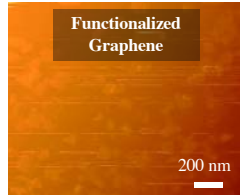
TEM of Graphene and Functionalized Graphene

Graphene from hyper-3-stage-1 GIC in DMF
Sonication overnight

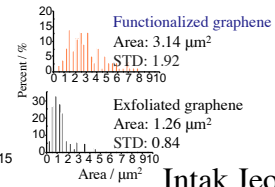
Functionalized graphene in MeCN
Sonication for 10 sec



AFM (Spincoating on Mica)

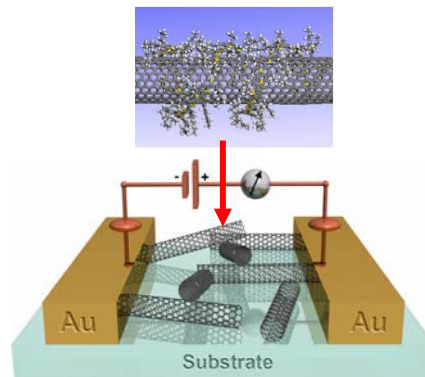


TEM (dropcasting)



Intak Jeon

CNT Chemiresistors



Advantages

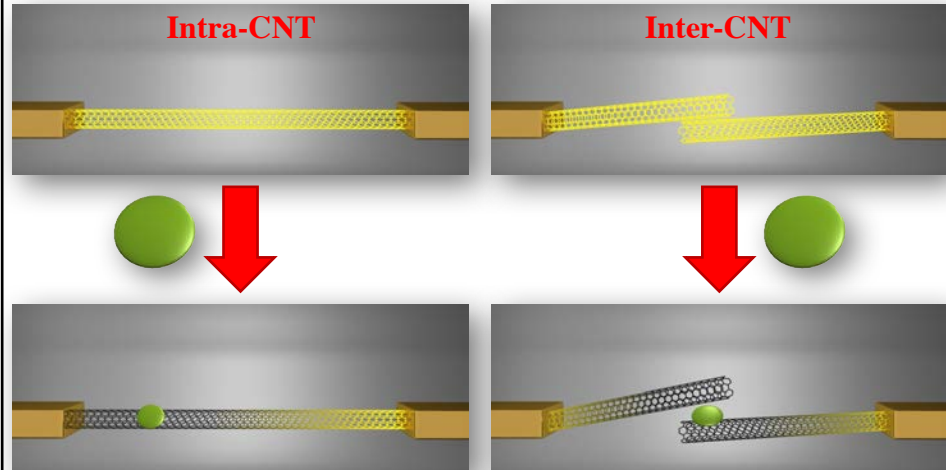
Low Power/Cost
Small Footprint
Wireless Network

Technical Needs

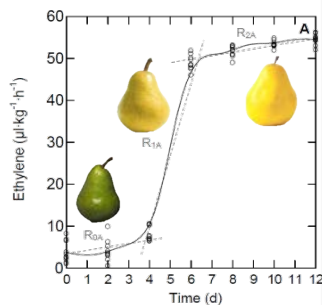
High Sensitivity
Selectivity
Minimize Drift

Carbon Nanotube Sensing Mechanisms

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



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)

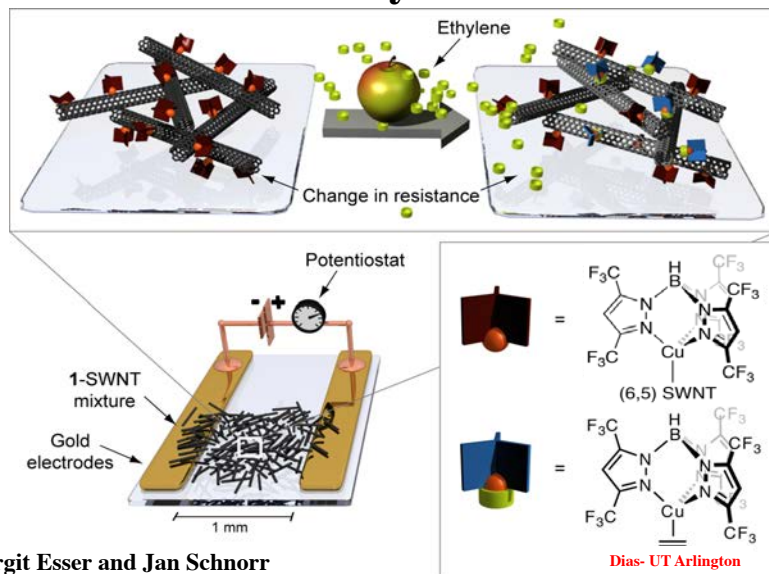
Amines:

- **Indicator of meat/fish spoilage**

Ammonia:

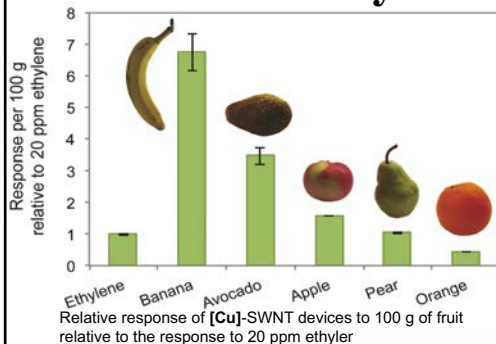
- **Soil nutrient level monitoring**

SWCNT-Based Ethylene Chemiresistors



Birgit Esser and Jan Schnorr
Angew. Chem. Int. Ed. **2012**, *51*, 5752-5756.

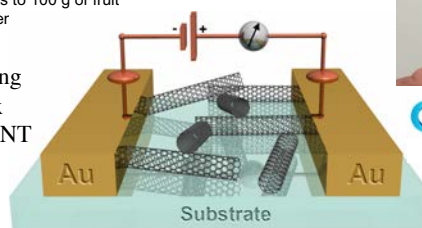
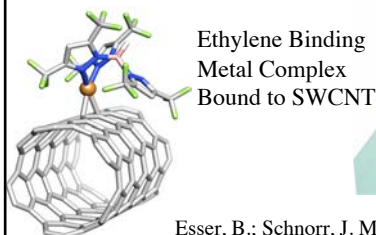
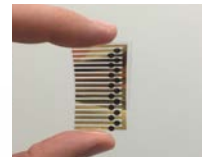
Detection of Ethylene Emissions from Fruit



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



SENSE

Esser, B.; Schnorr, J. M.; Swager, T. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 5752-5756.

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:

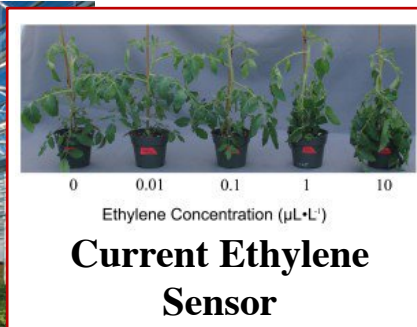
- Given off by produce during ripening
- Induces ripening/spoilage



Ethylene Sources



Protecting Plants in Greenhouses



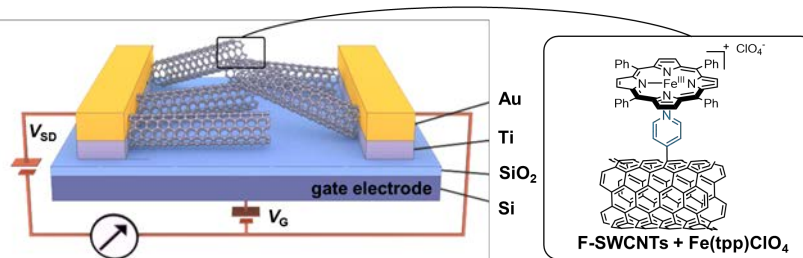
Ethylene:

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

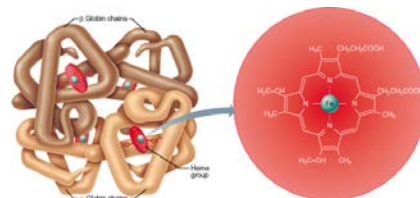
Better
Option



Bioinspired Gate Enhanced Sensors



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



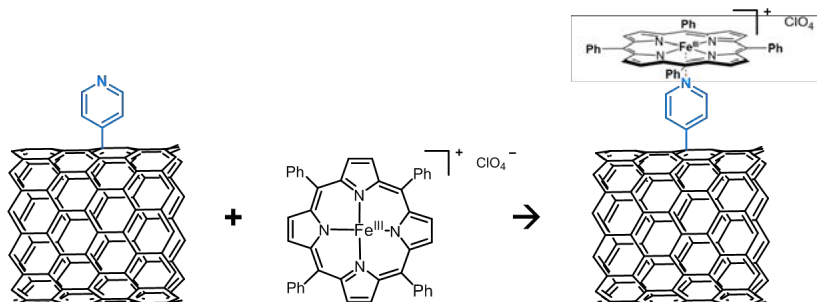
Hemoglobin

Heme group

"All About The Hemoglobin" By Shawn Koshy

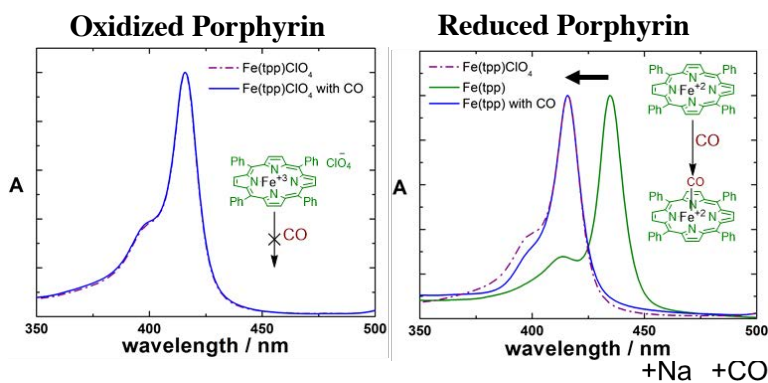
Hypotheses

- 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

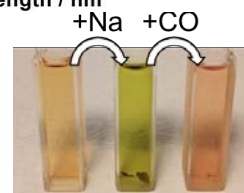


He, M.; Swager, T. M. "Covalent Functionalization of Carbon Nanomaterials with Iodonium Salts" *Chem. Mater.* **2016**, 28, 8542-8549.

Interactions between CO and $\text{Fe}(\text{tp})\text{ClO}_4$

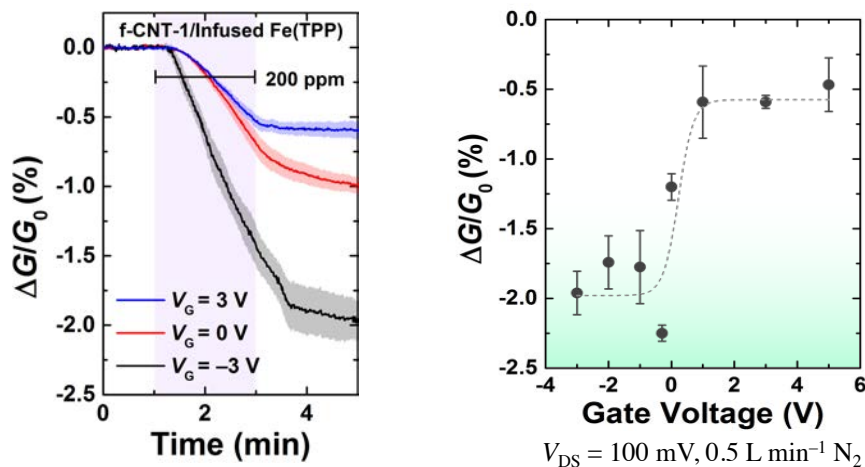


- Strong response from reduced porphyrin upon exposure to CO
- No response measurable in the UV-Vis of the oxidized porphyrin upon exposure to CO



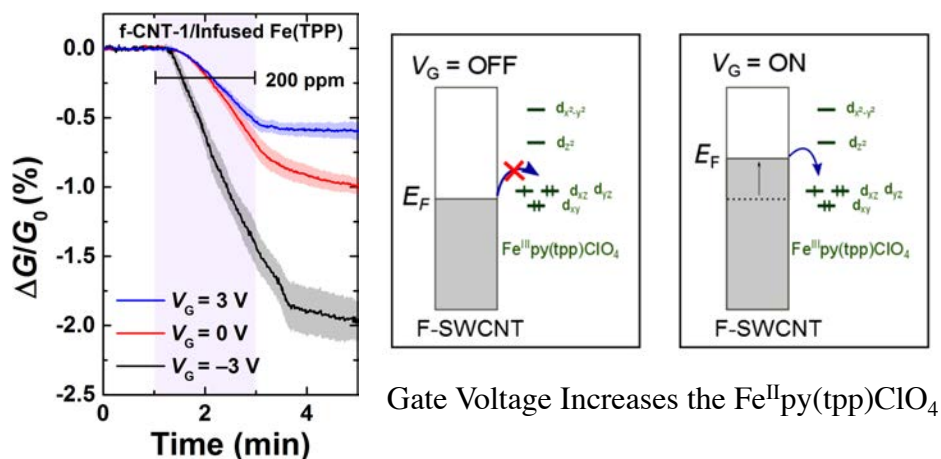
Suchol Savagatrup Vera Schroeder

Gate Voltage (V_G) Enhanced Sensitivity



Savagatrup, S.; Schroeder, V.; He, X.; Lin, S.; He, M.; Yassine, O.; Salama, K. N.; Zhang, X.; Swager, T. M. *Angew. Chem.* **2017**, *129* DOI: 10.1002/ange.201707491

Gate Voltage Enhanced Sensitivity



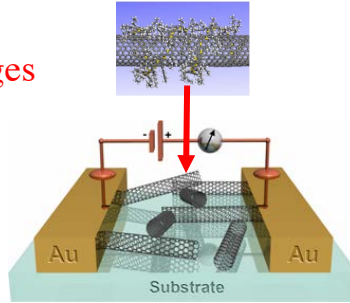
- Significant improvement in sensitivity towards CO for negative gate voltage
- Modulate the response using V_g

Suchol Savagatrup Vera Schroeder

CNT Chemiresistors

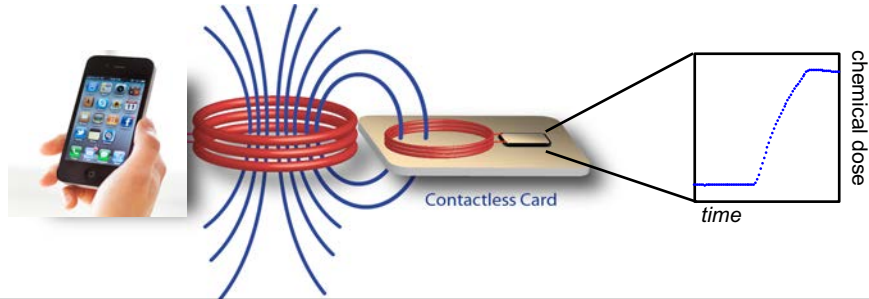
Intrinsic Advantages of Chemiresistors

- Low Power/Cost
- Small Footprint
- Wireless Network

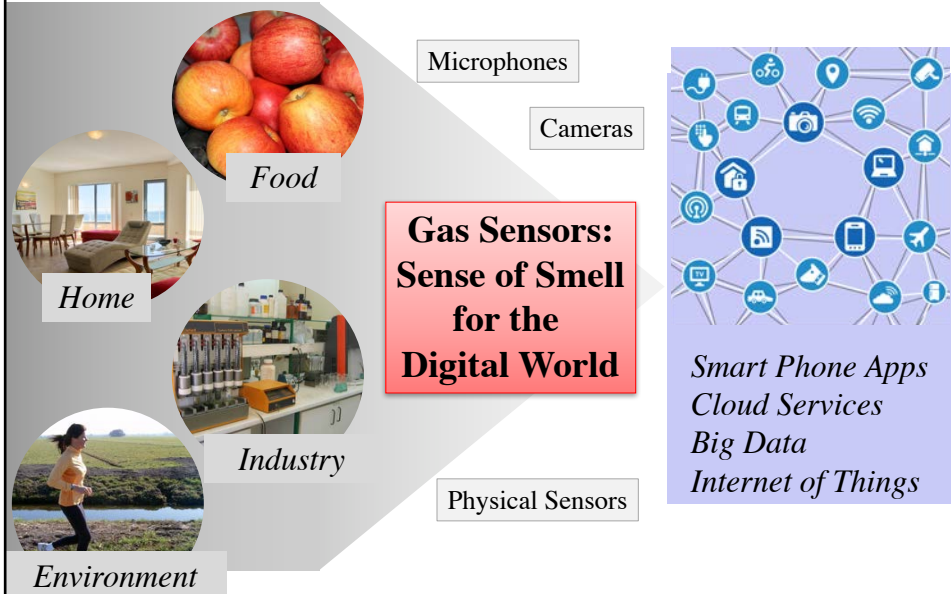


Technical Needs

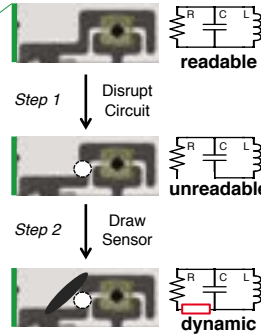
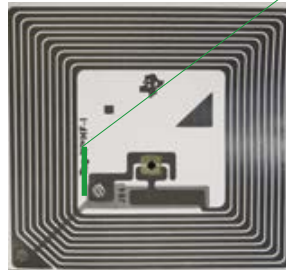
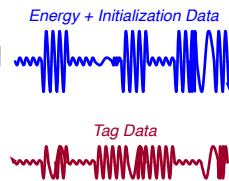
- High Sensitivity
- Selectivity**
- No Calibration



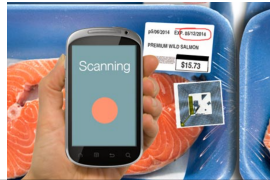
A Sense of Smell for the Digital World



Smartphone Sensing: Ultra-Low Power Wireless Sensors



Smart Packaging

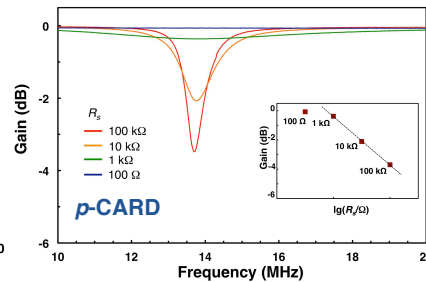
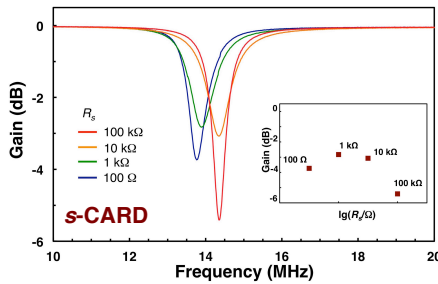
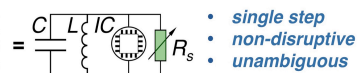
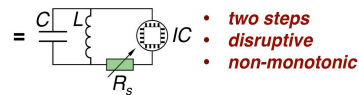
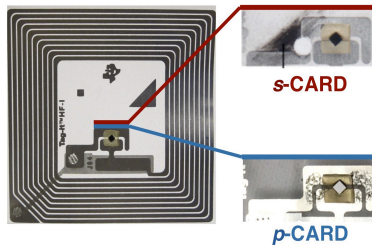


**Sensor Tags are
Inductively Powered
and Read by Smartphones**

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

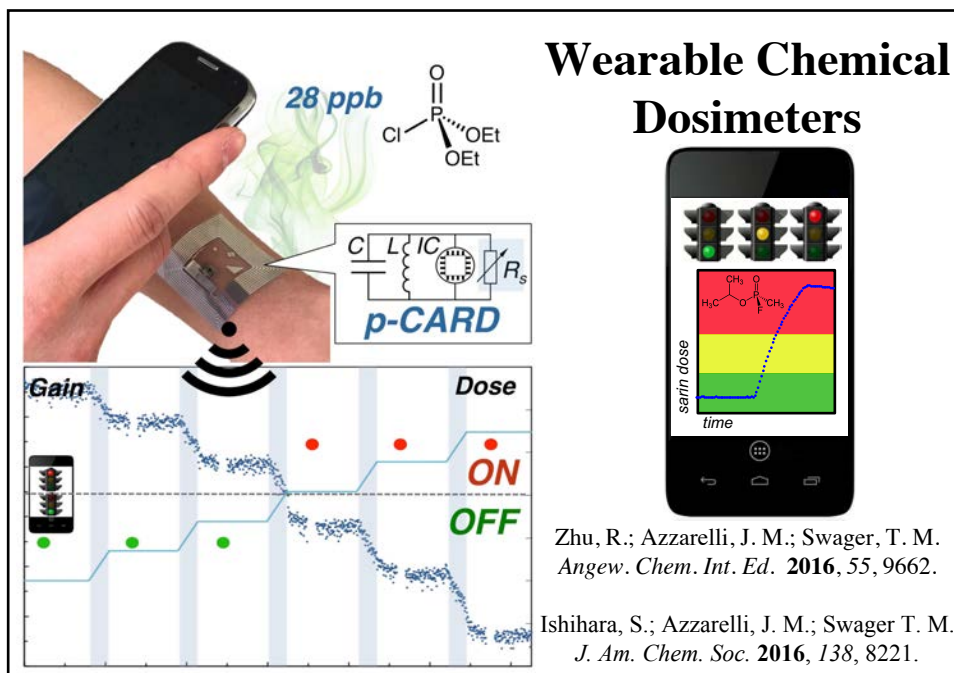
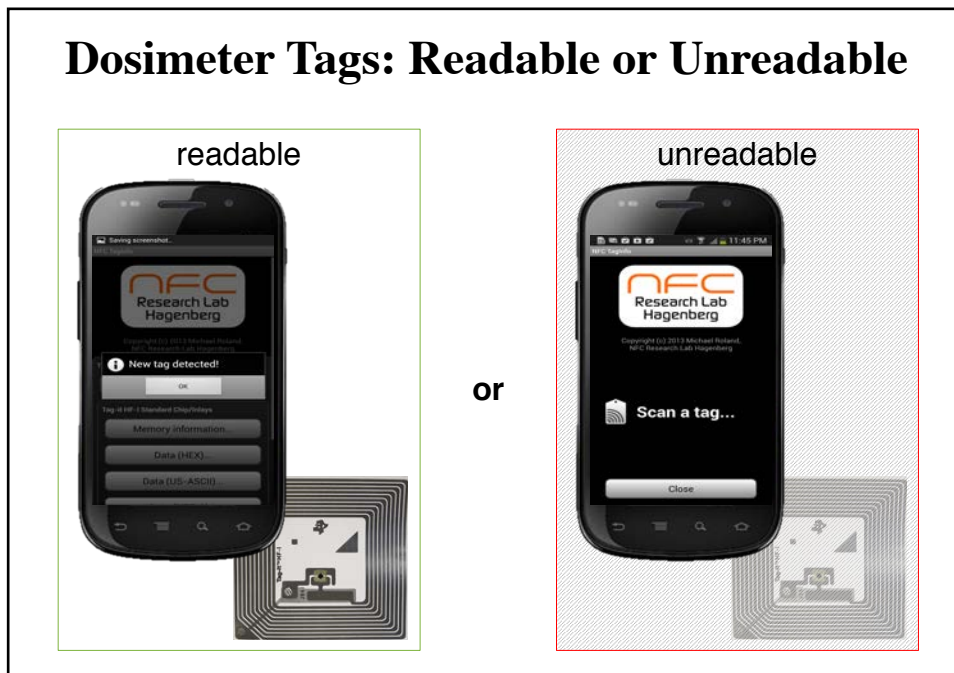
Azzarelli, J. M., Mirica, K. A., Ravnsbæk, J. B.; Swager, T. M.
Proc. Nat. Acad. Sci. **2014**, *111*, 18162-18166.

s-CARD vs. p-CARD



Rong Zhu, Joseph Azzarelli

Dosimeter Tags: Readable or Unreadable

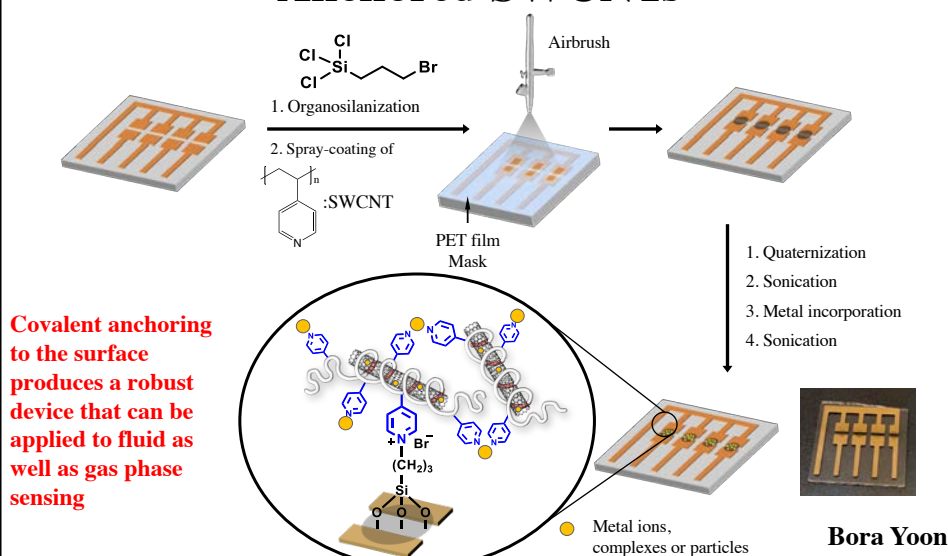


New Ways to Constrain CNT

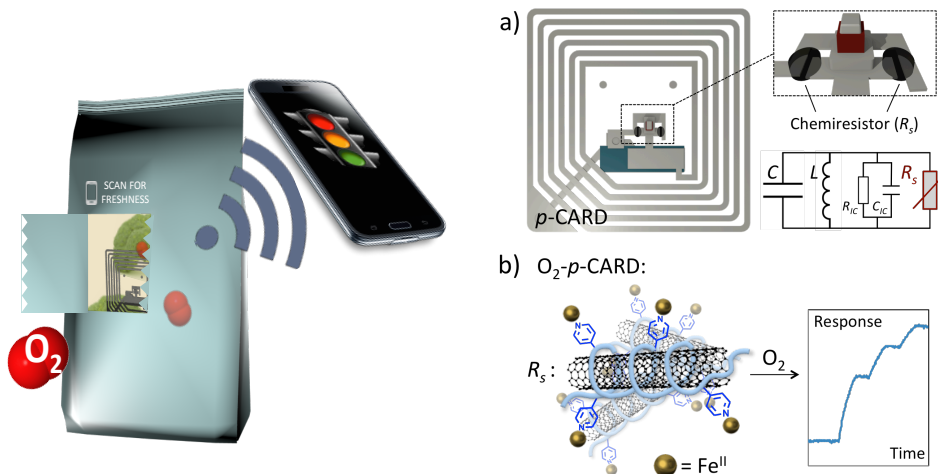
Non-Covalent Straps Anchored to the Surface



Fabrication of Sensor Devices with Surface Anchored SWCNTs



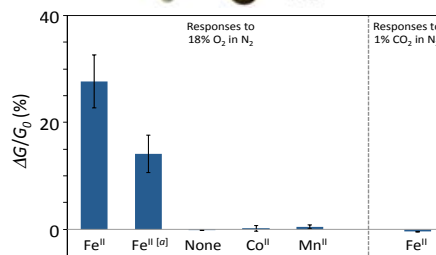
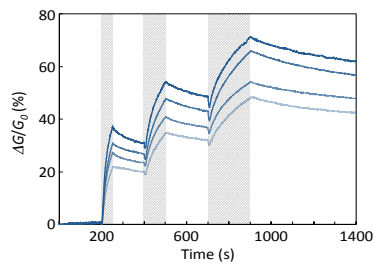
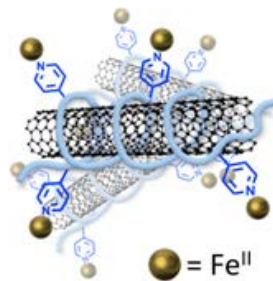
Food Packaging: Non-Line-of-Sight Detection of Freshness



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.

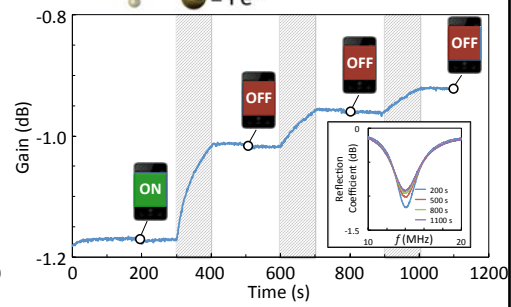
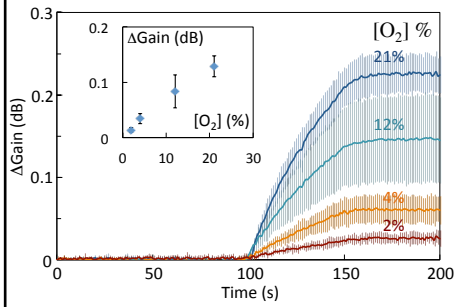
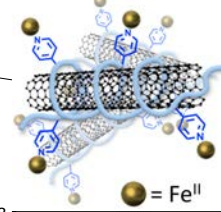
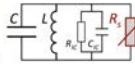
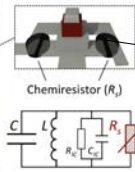
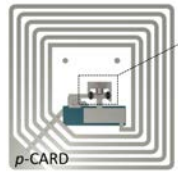
Sensor Formation and O₂ Response

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



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Passive RFID Tag Sensors and Smart Phone Digital Readout



Rong Zhu