Chemistry of the Graphene Surface for the Creation of Functional Nanomaterials

MIT ILP NanoTech Conf.
Timothy M. Swager

How Do You Make/Use Graphene?

1. Micomechanical Exfoliation
2. Epitaxial Growth
3. Chemical Exfoliation

Harsh Oxidation Conditions

GO in H₂O 1 mg/ml

Thermal/Chemical Reduction
The Problem...

- Re-aggregation of unstable graphene colloidal suspension
- Short "shelf-life" hinders large scale production / applications

C-O to C-C Transformations


Chem. Comm. 2011, 47, 8790-8792
N,N-dimethylacetamide dimethylacetal only reacts with the alcohols. Nitrogen (N 1s) incorporation can be quantified.


---

Transformation of Graphite Oxide

FTIR:

- C=O 1733 cm⁻¹
- C=C 1621 cm⁻¹
- C-OH 1226 cm⁻¹
- C-O 1053 cm⁻¹

Carboxylic acid

H₂SO₄, NaNO₃, KMnO₄

X-Ray Diffraction (XRD): 2.6 Carbons to 1 Oxygen

Graphite

William Collins and Wiktor Lewandowski
O to C Allylic Transposition in GO

\[ \text{Me}_2N\text{OMe} \xrightarrow{\text{Rearranged Material}} \text{Me}_2\text{O}\text{OMe} \]

(2 equiv/oxygen in GO)
THF, 60 °C, 24 h

Saponification of Modified Graphene Oxide

KOH, EtOH/H₂O
Reflux, 36 h

XPS:

N(1s):

1 Amide group per 22 carbons
1 Amide group per 83 carbons

Zeta Potential (at pH 11):

Increasing Charge
Graphene Acid-Base Chemistry

Highly Stable Colloidal Suspension (>5 mg/mL for 7+ months)

Graphenic Inks

<table>
<thead>
<tr>
<th>Spin Coated Films</th>
<th>Conductivity [S/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>Insulator</td>
</tr>
<tr>
<td>Carboxylic Acid</td>
<td>1.83</td>
</tr>
<tr>
<td>Carboxylic Acid</td>
<td>138.2</td>
</tr>
</tbody>
</table>

(Annealed 250 °C)

AFM Measurements (Tapping Mode): Sheets 0.5 nm Thick

William Collins and Wiktor Lewandowski
Reactions of GO with Less Reducing Carbanions

Graphite Oxide + (NC)₂CH⁻Na⁺ → Graphene Derivative

Alkylation

Graphite Oxide

Graphene Derivative

H₂O

SO₃⁻Na⁺

DCB

Electrochemical Graphene Exfoliation

Functional Graphene w/o Added Oxygen Defects

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

Solvent Molecules Co-intercalate with Li⁺

Graphite Intercalated Compounds (GIC, Liₓ(solv)ᵧCₙ)

Electrochemical Exfoliation/Expansion of Graphite


Electrochemical Activation of HOPG

Final potential $-2.22\text{V }\text{vs }\text{Ag/Ag}^+$
Staged Electrochemical Graphene Synthesis

HOPG Starting Material

-2.2 to -2.7 V (vs Ag/Ag+)
TBA+/DMF/MeCN
Full stage-1 GIC ($d_{001} \sim 8.17 \text{ Å}$)

-2.2 to -2.8 V (vs Ag/Ag+)
TBA+/DMF/MeCN
Hyper-1-stage-1 GIC ($d_{001} \sim 12.7 \text{ Å}$)

-2.8 to -2.9 V (vs Ag/Ag+)
TBA+/DMF/MeCN
Hyper-2-stage-1 GIC ($d_{001} \sim 15.3 \text{ Å}$)

Intak Jeon

XRD of Graphene Intercalation Compounds

Functionalized graphene

Hyper-3-stage-1 GIC
Disordered

Hyper-2-stage-1 GIC ($d_{001} \sim 15.3 \text{ Å}$)

Hyper-1-stage-1 GIC ($d_{001} \sim 12.7 \text{ Å}$)

Stage-1 GIC ($d_{001} \sim 8.17 \text{ Å}$)

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

WE: Graphite
Electrochemical Potential

TBA⁺ ion
Functional Group
Solvent/Amine

Mechanical Force
Defect Free Exfoliated Graphene

Chemical Functionalization
Functionalized Graphene

Intak Jeon

Spontaneous Reactive Exfoliation

HOPG ($d_{002} \approx 3.35 \text{ Å}$)
TBA⁺
Reduced TBA⁺
Functional group

Hyper-3-Stage-1 GIC
(Disordered $d_{002}$)

< -3.05 V (vs Ag/Ag⁺)
TBAP/DMF/MeCN

< -1.2 V (vs Ag/Ag⁺)
Diazonium salt/TBAP/MeCN

Spontaneous exfoliation of functionalized graphene

In diazonium/TBAP/MeCN
Raman Characterization

- Doping
- Strain
- e-doping
- Raman shift / cm⁻¹
- Ratio of ID/IG
- G-band
- D-band
- 2D-band

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
  - NO₂
  - 3,5-Dinitrobenezene diazonium salt
  - N=N - NH₂

- XPS C1s
  - sp³ C-C
  - Functionalized Graphene
  - Binding energy / eV
  - Raman
    - 1200 - 1600 - 2000
    - 2D
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)

Functionalized Graphene

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

Intra-CNT

Inter-CNT

Gases in Food Management

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

Dias - UT Arlington
Birgit Esser and Jan Schnorr

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

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

Apple Cold Storage Facilities: $1M in Each Room

Protecting Plants in Greenhouses

Ethylene Sources

Ethylene:
• Given off by produce during ripening
• Induces ripening/spoilage

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 C-Sense, 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.
Protecting Plants in Greenhouses

Ethylene:
• Given off by produce during ripening
• Induces ripening/spoilage

Current Ethylene Sensor

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 \textit{in situ}
- The reduction of Fe$^{3+}$ to Fe$^{2+}$ will enhance CO detection


Interactions between CO and Fe(tpp)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

- 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**

- **Gas Sensors:** Sense of Smell for the Digital World
- **Smart Phone Apps**
- **Cloud Services**
- **Big Data**
- **Internet of Things**

- **Food**
- **Home**
- **Industry**
- **Environment**
Smartphone Sensing:
Ultra-Low Power Wireless Sensors

Sensor Tags are Inductively Powered and Read by Smartphones

Azzarelli, J. M., Mirica, K. A., Ravnsbæk, J. B.; Swager, T. M.

s-CARD vs. p-CARD

Rong Zhu, Joseph Azzarelli
Dosimeter Tags: Readable or Unreadable

Wearable Chemical Dosimeters

New Ways to Constrain CNT

Non-Covalent Straps Anchored to the Surface

Fabrication of Sensor Devices with Surface Anchored SWCNTs

Covalent anchoring to the surface produces a robust device that can be applied to fluid as well as gas phase sensing.

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


Sensor Formation and O₂ Response

- Response to 18% O₂ in N₂
- Dosimeter Behavior
- No CO₂ Response
- Co²⁺ and Mn²⁺ are Ineffective

Rong Zhu, Bora Yoon, Maude Desroches
Passive RFID Tag Sensors and Smart Phone Digital Readout

Rong Zhu