Chemically Refined Carbon Nanomaterials

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Unlike bulk materials, nanomaterials possess:

1. Exceptionally high surface area to volume ratio
   - Surface chemistry/passivation is paramount since adsorbates can modify properties.

2. Size/shape-dependent properties
   - Any polydispersity in structure leads to inhomogeneity and/or irreproducibility in properties.
Introduction to Carbon-Based Nanomaterials


- **2-D:** Graphene
- **0-D:** Fullerene
- **1-D:** Nanotube
- **3-D:** Graphite
Lecture Outline

Carbon-based nanomaterials at multiple length scales:

Atomic scale:
Functionalization and characterization of graphene

Nanometer scale:
Monodisperse carbon nanotubes and graphene in solution

Micro/macro scale:
Carbon nanotube and graphene thin film materials and devices
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Graphene Functionalization Motivation


- The superlative and exotic electronic properties of graphene have been widely studied in condensed matter physics.
- However, the surface chemistry of graphene is relatively unexplored.
- In addition to serving as a seeding layer for materials growth, chemical functionalization of graphene holds promise for tailoring electronic properties (e.g., doping, band gap control, etc.)
SiC(0001) graphitized by annealing in UHV at ~1350°C
Defect density and relative amount of SLG, BLG, and $6\sqrt{3}$ depend on the details of the UHV processing
Surface Chemistry of Epitaxial Graphene


- Substrate: n-type SiC(0001)
- Graphitized by repeated annealing in UHV at ~1200°C for 30 s
- Preparation conditions were chosen to yield a variety of surface defects to determine their influence on subsequent chemistry
PTCDA
(3,4,9,10-perylene-tetracarboxylic acid dianhydride)


- Perylene-based molecule that forms ordered adlayers on graphite via noncovalent bonding (preserves sp² hybridization of graphene)
- Thermally stable \( \Rightarrow \) amenable to gas phase processing
- Crystalline molecular semiconductor that has been widely studied for organic thin film device applications
PTCDA Monolayer on Epitaxial Graphene


June, 2009

- Gas phase deposition of a monolayer of PTCDA
- Stable herringbone phase achieved at room temperature
- Long range order is observed including seamless continuity in molecular ordering over step edges
Tunneling spectra reconfirm weak interaction between PTCDA and graphene (i.e., PTCDA imparts chemical functionality with minimal electronic perturbation)
Seeding Atomic Layer Deposition on Graphene

• Monolayer of PTCDA can seed ALD growth of dielectrics on graphene
• Other gas phase and liquid phase chemistries are under development


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Metal/Oxide/Graphene Capacitor Structures


- Dielectric structure: PTCDA + 3 nm ALD Al₂O₃ + 10 nm ALD HfO₂
- AFM and SEM confirm highly conformal growth of dielectric stack
• Low pinhole density and leakage current for 100 µm test structures
• Capacitance measurement implies $k_{\text{alumina}} = 5.6$ and $k_{\text{hafnia}} = 13$
• Low hysteresis suggests low interface trap density
• Preliminary FET measurements show minimal degradation in mobility following top gate dielectric deposition
PTCDI-C8 Monolayers on Epitaxial Graphene


N,N'-dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8)

- Self-assembled monolayers of PTCDI-C8 on epitaxial graphene show different ordering than PTCDA
Nanopatterning with UHV STM

*Annual Review of Physical Chemistry, 60, 193 (2009).*

- STM can be used to pattern variety of chemical resist layers and isolated molecules
- Tip-induced desorption via electronic excitation or vibrational heating

**Hydrogen on Si(100)**

**SAM on Au(111)**

**Cyclopentene on Si(100)**
Feedback Controlled Lithography of PTCDA

*Nano Letters, 11, 589 (2011).*

- Control and reproducibility of patterns greatly improved by using feedback controlled lithography to selectively desorb PTCDA domains that are ≈2 nm diameter.
PTCDA as a Chemical Resist on Graphene

Heteromolecular Nanopatterns on Graphene


- Heteromolecular nanopatterns implemented with PTCDA resist and PTCDI-C8 insert
- Molecular ordering is observed in the PTCDI-C8 nanopatterns
Covalent Chemistry on Epitaxial Graphene

\[ \text{JACS 1992, 114, 5883; Chem. Mater. 2006, 18, 2021; JACS 2009, 131, 1336.} \]

Reaction scheme for aryl diazonium salt:

- Covalent functionalization of graphene recently demonstrated via reduction of aryl diazonium salt in solution
- Disruption of graphene sp\(^2\) hybridization influences electronic properties
- Radical mediated chemistry may lead to polymerization
UHV STM of Covalently Arylated Graphene

*Journal of the American Chemical Society, 132*, 15399 (2010).

SiC-graphene dipped into 4-nitrophenyl diazonium salt solution in glove box followed by degassing at 500ºC in UHV

- Strong evidence for polymerization
- Robust in atmosphere
- Local perturbation to electronic properties at covalent binding sites
STS on Covalently Arylated Bilayer Graphene

- Clean bilayer graphene shows a minimum in $\frac{dI}{dV}$ at -0.3 V (i.e., n-type)
- On the arylated surface, the minimum at -0.3 V is not observed but finite $\frac{dI}{dV}$ is still present at all biases
- In a small number of cases (~5%), a band gap is observed on the arylated surface (presumably at covalent binding sites)

*Journal of the American Chemical Society, 132, 15399 (2010).*
Covalently Modifying Graphene with Atomic Oxygen

*Nature Chemistry, 4, 305 (2012).*

- Atomic oxygen is generated in UHV by cracking molecular oxygen on a hot (~1500°C) tungsten filament.
- Bright protrusions are attributed to chemisorbed oxygen species.
Uniformity of features in STM implies one primary binding configuration.

Comparison with DFT calculations suggests epoxy functionalization.

*Nature Chemistry, 4, 305 (2012).*
Reversible UHV Oxidation and Reduction

*Nature Chemistry, 4, 305 (2012).*

- Oxidation is fully reversible upon thermal annealing or STM lithography.

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**Annealed at 260 °C**

**O dosed at room temp.**

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**Atomic scale:**
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Monodisperse carbon nanotubes and graphene in solution

**Micro/macro scale:**
Carbon nanotube and graphene thin film materials and devices
Carbon Nanotube Polydispersity


- Current synthetic methods yield polydisperse mixtures of CNTs.
- Post-synthetic methods for sorting by diameter, electronic type, chiral handedness, and number of walls are highly desirable.
Density Gradient Ultracentrifugation (DGU)


A preformed density gradient is used, and nanotubes move until their density matches that of the local density of the gradient.

**Attributes of DGU**

- Compatible with any raw material
- Highly reproducible and predictable
- High purity sorting by essentially all structural and electronic parameters
- Proven industrial scalability
- Enhances performance of electronics, sensors, optoelectronics, transparent conductors, etc
- Generalizable to a diverse range of nanomaterials
- Compatible with a wide array of chemistries (surfactants, polymers, etc)
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Isopycnic Separation by SWCNT Diameter

Separation by SWCNT diameter occurs when using a one component surfactant (e.g., sodium cholate)

Electronic Type Separation with Co-Surfactants


Metal and semiconductor purities exceeding 99% are routinely achieved using co-surfactants.
Circular dichroism reveals enantiomer sorting for CoMoCAT SWCNTs encapsulated with sodium cholate
Toward Single Chirality: Ultrapure (6,5) SWCNTs

*Advanced Materials, 23, 2185 (2011).*

Multiple orthogonal DGU iterations yield relatively large quantities of ultrapure (6,5) SWCNTs from HiPco raw material.
Resulting Ultrapure (6,5) SWCNTs

Attributes of ultrapure, enantiomerically enriched (6,5) SWCNTs:
- Semiconductor purity > 98%
- 99% of species within 0.01 nm diameter range
- Sufficient quantities for prototype device fabrication
Scalability of Density Gradient Ultracentrifugation

http://www.nanointegris.com/

~10,000x scale up of metal and semiconductor IsoNanotubes™ and graphene PureSheets™; 450+ customers in 40+ countries
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A preformed density gradient is used, and nanotubes move until their density matches that of the local density of the gradient.
Electronics with Semiconductor SWCNT Films

1 mA drive current FETs

ACS Nano, 4, 4388 (2010).
Printed digital circuits

APL, 94, 243505 (2009).
80 GHz RF electronics

Hydrogen sensors
Optoelectronics with Semiconductor SWCNT Films


Optics Express, 18, 25738 (2010).

Near-infrared electroluminescence from ambipolar FETs

Polarized near-infrared emission from aligned light-emitting diodes
Applications for Metallic SWCNT Films

*Visibly colored translucent conductors*

*Phonon-mediated electroluminescence from metallic SWCNTs and graphene*

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**Nano Letters, 8, 1417 (2008).**

**Nano Letters, 10, 1589 (2010).**
Monodisperse SWCNTs in Organic Photovoltaics


Metallic SWCNT anodes outperform semiconducting SWCNTs by 50x in power conversion efficiency in PEDOT:PSS/P3HT:PCBM OPVs.
Density Gradient Ultracentrifugation (DGU)

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*Nano Letters, 5, 713 (2005).*
Isolating Double-Walled Carbon Nanotubes

DWCNTs isolated from SWCNTs and MWCNTs via 2-step DGU

DWCNTs sorted by outer shell electronic type


Graphene Polydispersity


Graphene properties depend on:

- Number of graphene layers
- Lateral area
- Nanoribbon width

Structurally monodisperse graphene samples are required for many fundamental studies and applications.

January, 2010
DGU of Graphene

Nano Letters, 9, 4931 (2009).

- Exfoliate graphite powder via sonication in aqueous solution with the planar surfactant sodium cholate.
- DGU enables sorting by the number of graphene layers.
GHz Flexible Transistors from DGU Graphene

Nano Letters, 12, 1184 (2012).
Collaboration with Vincent Derycke (CEA Saclay) and Henri Happy (UMR-CNRS)

- 2.2 GHz $f_T$ before de-embedding
- 8.7 GHz $f_T$ after de-embedding
- 1000x faster than alternative solution processable organic materials
Graphene-Based Hole Transport Layer in OPVs


- UV ozone oxidized graphene is an effective replacement for PEDOT:PSS as a hole transport layer in PTB7:PC$_{71}$BM OPVs.
- PCE = 7.5%; environmental stability improved by 20-fold.
Transient DGU of Plasmonic Nanoantennas


**Raw material:**
~100 nm Au nanoparticles with ~60 nm silica shell

Transient DGU using high viscosity density gradient media (e.g., iodixanol) allows relatively massive, high density nanoparticles to be separated by aggregation state, thus enhancing plasmonic activity such as SERS.
Density Gradient Ultracentrifugation (DGU)

A preformed density gradient is used, and nanotubes move until their density matches that of the local density of the gradient.


Attributes of DGU

• Compatible with any raw material
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• Generalizable to a diverse range of nanomaterials
• Compatible with a wide array of chemistries (surfactants, polymers, etc)
Beyond Surfactants: Biocompatible Polymers

*Nano Letters, 10, 1664 (2010).*

Collaboration with Scott Budinger and Gokhan Mutlu (NU Medical School)

<table>
<thead>
<tr>
<th>Pluronic Control</th>
<th>24 hours</th>
<th>30 Days</th>
<th>90 Days</th>
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<tbody>
<tr>
<td>Nanoscale dispersed SWCNT</td>
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In vivo pulmonary toxicity in mice drops to undetectable levels when SWCNTs are well dispersed using biocompatible polymers (e.g., poloxmers)
Pluronic and Tetronic Block Copolymers

ACS Nano, 4, 4725 (2010).

- Pluronic and Tetronic block copolymers have tunable hydrophilic (PEO) and hydrophobic (PPO) segments
- Nonionic character has potential advantage for electronic and electrochemical applications
DGU with Pluronic Encapsulated SWCNTs

ACS Nano, 4, 4725 (2010).

- Pluronics isolate semiconducting SWCNTs in DGU
- Banding pattern and SWCNT purity depend on block copolymer structure (semiconductor purity increases with decreasing PPO length)
DGU with Tetronic Encapsulated SWCNTs

ACS Nano, 4, 4725 (2010).

- Tetronics effectively disperse SWCNTs (better than SDS)
- Tetronics isolate metal SWCNTs in DGU
Pluronics/Tetronics also Disperse Graphene

Dispersion efficiency of graphene depends on the molecular weights of the hydrophobic (PPO) and hydrophilic (PEO) blocks.

*Journal of Physical Chemistry Letters, 2, 1004 (2011).*
Minimizing Toxicity of Graphene with Pluronic


Pluronic-dispersed graphene shows significantly reduced toxicity compared to aggregated graphene or graphene oxide.
Highly Concentrated Graphene in Organic Solvents


• Use of a stabilizing polymer (ethyl cellulose) increases the concentration of graphene in ethanol by ~100-fold.

• Iterative solvent exchange with terpineol and water increases the graphene concentration by another factor of 10 (~1 mg/mL) without centrifugation.

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Graphene-Titania Nanocomposites

*Nano Letters, 11, 2865 (2011).*

Combined to form Nanocomposites

Graphene-TiO$_2$ from 67.9 - 99.6 %TiO$_2$

SWCNT-TiO$_2$  RGO-TiO$_2$
Graphene-Titania Nanocomposite Photocatalysis

*Nano Letters, 11, 2865 (2011).*

Photocatalytic Reduction of Carbon Dioxide to Methane

7-fold improvement in CH$_4$ production with visible light for solvent-exfoliated graphene/titania nanocomposites
• Chemical refinement adds significant value to carbon-based nanoelectronic materials and devices.

• Monodispersity in structure and surface chemistry enables improved properties in a diverse range of applications.
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<tr>
<th>Postdocs/Scholars</th>
<th>Graduate Students</th>
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