Opto-electronic Properties of Graphene Oxide and Partially Oxidized Graphene

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Forms of Carbon

Diamond, circa 4000 BC
In India

Graphite, ~ 1550
Great Britain

C60, 1985

SWNTs in 1993

Graphene, 2004

armchair
zigzag
chiral

3 - D

1 - D

2 - D

0 - D
Electronic structure of graphene

Dispersion relation using Tight Binding:

\[ E(k_x, k_y) = \pm \gamma_0 \left[ 1 + 4 \cos\left(\frac{\sqrt{3}k_x a_{C-C}}{2}\right) \cos\left(\frac{k_y a_{C-C}}{2}\right) + 4 \cos^2\left(\frac{k_y a_{C-C}}{2}\right) \right]^{1/2} \]

\[ E = \hbar v_F k \]

Dirac cone
Why Graphene?

- Chemical, mechanical, and thermal stability
- 0 eV band-gap semiconductor
  - Ambipolar field effect transistors
- Extraordinary mobility
  - Room temperature mobility of \( \sim 10,000 \text{ cm}^2/\text{Vs} \)
- High current carrying capability
  - Electrons and holes up to \( 10^{13}/\text{cm}^2 \)
- Exotic physical properties
  - Relativistic charge carriers – massless Dirac Fermions
  - Unusual quantum Hall effect
  - Ballistic transport
Graphene: Challenges

Graphene science is exciting...
Graphene properties are remarkable...
BUT for technological implementation
- Technologically viable deposition method
- Control over deposition areas
- Choice over substrate
- Control over the number of graphene layers
- Reliable growth method

Graphene on Copper

Li et al, Science (2009)

“Graphene Inks?”

Graphite → Exfoliation → Thin film deposition

Graphite → “Graphene ink” → “Solution-based deposition”
“Graphene Inks?”

Graphite is insoluble!!

“Solution-based deposition”
XIII. On the Atomic Weight of Graphite. By D. C. Brodie, F.R.S., Professor of Chemistry in the University of Oxford, and President of the Chemical Society.

Received May 12—Read May 12, 1859.

The term Graphite has been indiscriminately applied to many varieties of native carbon of very different properties. The graphite of New Brunswick differs but little in appearance from anthracite coal. The graphite of Greenland is not very dissimilar, but possesses rather more metallic lustre. However, among these varieties of carbon, two may be especially distinguished,—by a superior degree of metallic lustre, by their structure, and other well-defined properties. In the following paper, the term Graphite is limited to these two varieties, which may be further distinguished as "lamellar" and "amorphous."

These crystals, when examined with the microscope, are perfectly transparent, and exhibit beautiful colours by the agency of polarized light. Professor Miller of Cambridge, who was good enough to examine them, has communicated to me the following observations:—"The crystals, though not absolutely too small to be measured, are too thin and too imperfect to admit of measurement with the reflective goniometer. I have examined them under a microscope, for the purpose, if possible, of making out at least the system of crystallization to which they belong. Their system appears to be either..."
What is Graphene Oxide?

Graphite powder

- $2/kg

Some of Our Contributions:
- Nano Letters 9, 1058 (2009)
- Adv Funct Mat 19, 2577 (2009)
- ACS Nano 4, 524 (2010)
- Advanced Materials 22, 2392 (2010)

Graphite oxide

Colloidal suspension

GO: thin films

OXIDATION: Hummers-Offman (1958)
(NaNO₃, KMnO₄, H₂SO₄)

Brodie (1859)
Staudenmier (1898)
Hofmann-Frenzel (1930)
Hofmann-Konig (1937)
Ruoff et al. (2006)
Variable Oxidation

GO ~ 30% Oxygen
rGO ~ 7 – 8 % Oxygen

POG ~ 10 – 12% Oxygen
rPOG ~ 2 – 3 % Oxygen

~ 30 % sp²
~ 70 % sp²
~ 90 % sp²
Graphene Oxide

1. As-Synthesized GO: sp$^3$ = 60%
2. Solution Processable
3. Can be produced in ton quantities

Flake sizes: Few microns up to 100µm.

Distribution of oxygen in GO is highly non-uniform, with approximately 2-3 nm domain of very high oxidation and sparse oxidation.

\[
\frac{I(D)}{I(G)} \sim 2.4 \text{ nm}
\]

High-magnification Annular Dark Field image of monolayer GO.

Simulation by multislice computational method.


“Tunable” opto-electronic properties

Increasing filtration volume

Reduce

Thin Thick

Raman mapping

# of layers

- >5
- 3-5
- 2
- 1

50x objective

monochrometer

CCD

Reduced GO thin film

20 mL film (very thin)

80 mL film (thicker)

N = 0.037 \times V + 0.735

Filtration volume (mL)

Number of layers

12 in. (300mm) Wafer Scale Deposition

μ > 10 cm²/V-s up to 300 cm²/V-s
Reduced GO: open questions

- How does the GO structure (chemical, atomic, electronic) evolve upon reduction?
- How do the properties (optical, electrical) evolve upon reduction?
- What are the limiting factors for mobility and conductivity of rGO?
  - How much oxygen can be removed? In which form is the residual oxygen present?

Monolayer reduced GO

- **mobility**: Up to 100 – 300 cm²/Vs
  - **on/off ratio**: 2~100
- **sheet resistance**: ~ 1 kΩ/sq
Evolution in electronic structure

Sheet conductivity (1/MΩ)

Reduction time (hr)

1 10 100 1000 (min)

0.01 0.1 1 10 100

Insulator

Semi-metal

?
Rate of oxygen release

Initial Oxygen 40 at.%

150 °C Oxygen 27 at.%

Final Oxygen 8 at.%

Evolution of structure with reduction

(a) 20%
(b) 25%
(c) 33%
(d)
(e)
(f)
Pyran formation

Hydroxyls-epoxies

(a) Loss of CO$_2$

(b) Loss of CO

epoxy-epoxy

(c) (d)

Hydroxyl - Epoxy interplay lead to…

Oxygen functional groups and carbon arrangements after annealing

(a) pair of carbonyls, (b) carbon chain, (c) pyran, (d) furan, (e) pyrone, (f) 1,2-quinone, (g) 1,4-quinone, (h) carbon pentagon, (i) carbon triangle, (j) phenol. Carbon, oxygen and hydrogen atoms are color-coded as gray, red and white, respectively.
Giant IR Effects in rGO

In collaboration with Muge Acik and Yves Chabal at UT – Dallas (Nature Materials, 9, 840 2010)
“Tunable” Opto-electronic Properties

Structure of GO

\[ L_a = \left[ 2.4 \times 10^{-10} \text{ nm}^{-3} \right] \lambda^4 \left( \frac{I_D}{I_G} \right)^{-1} \]

\[ L_a \sim 2 \text{ nm} \quad \text{“Domain size”} \]
Direct observation of sp2 clusters

As-synthesized GO
Direct observation of sp2 clusters

After mild-reduction
Progressive reduction

Transfer characteristics

\[ V_{sd} \quad I_{sd} \]

\[ \text{Graphene oxide flake} \]

\[ \text{SiO}_2 \quad \text{Si} \]

\[ V_g \]

\[ T = 78 \text{ K} \]

\[ T = 300 \text{ K} \]

Carrier transport via hopping

In 2D system, VRH is described by:

\[ \sigma = A \exp \left( -\frac{B}{T^{1/3}} \right) \]

\[ A = \frac{e R_0^2 \nu_{ph}}{k_B} \]

\[ B = \left( \frac{3}{N(E_F) L_i^2 k_B} \right)^{1/3} \]

DOS at \( E_F \)  
Localization length

\[ \sigma_{\text{min}} (\sigma^{-1}) \]

\[ T^{-1/3} \text{ (K}^{-1/3}) \]

\[ V_g = \sim 0 \text{ V} \]

At the charge neutrality point,

\[ n_e = n_h = n_i \]

\[ \sigma_{\text{min}} = e n_i (\mu_e + \mu_h) \]
Evolution of the electronic structure

At low T,\[
\frac{\partial n_i}{\partial T} = N(E_F)k_B
\]

\[
B = \left( \frac{3}{N(E_F)L_l^2k_B} \right)^{1/3}
\]

obtain \( N(E_F) \) and \( L_l \)

\( \rho_{\text{max}}^{RT} (h/e^2) \)

\( N(E) \)

Before reduction

After reduction

Coherence length (sp\(^2\) cluster size) estimated from Raman analysis.

Structure of GO

![Graphene Sheet Images]

\[ L_a = \left[2.4 \times 10^{-10} \text{ nm}^{-3}\right] \lambda^4 \left(\frac{I_D}{I_G}\right)^{-1} \quad \Rightarrow \quad L_a \sim 2 \text{ nm} \quad \text{“Domain size”} \]
Tunable fluorescence
Progressive reduction

- Change in conduction mechanism
- VHR
- Tunneling

- Percolation
- No percolation
Optical and electrical property correlation

Absorbance

PL intensity

Conductivity

The sp² phase of GO becomes percolating after ~ 10 min of exposure to hydrazine
Mild oxidation, intercalation, and exfoliation of graphite

Brodie’s method

Graphite + HNO₃ + KClO₄

Electrical properties

As-synthesized POG

Reduced POG

σ(1/Ω)

Graphene

POG

GO
Single flake vs “poly-flake” thin film

**Single flake**

- $V_D = 20$ mV
- $\sigma = 20 - 100 \text{ cm}^2/\text{Vs}$
- $R_s \sim 26.8 \text{ k}\Omega/\text{sq}$

**Thin film (~1.5 layer)**

- $V_D = 20$ mV
- $\sigma = 2 - 50 \text{ cm}^2/\text{Vs}$
- $R_s \sim 23.4 \text{ k}\Omega/\text{sq}$
Field effect mobility (individual sheet)

![Graph showing field effect mobility (cm²/Vs) for different samples at various temperatures.](image)

- GO
- POG

- 400°C: 0.01 cm²/Vs
- 800°C: 0.1 cm²/Vs
- 1000°C: 1 cm²/Vs
- N2H4 + 400°C: 1.1 cm²/Vs
- N2H4 + 800°C: 10 cm²/Vs
- Vitamin C: 250°C: 100 cm²/Vs

**References:***
- Dong et al. PCCP (2010)
- Su et al. ChemMat (2009)
- Our work
Patterning of graphene films

I. UV exposure

II. Graphene deposition

II. Develop resist/lift-off

OTFT with graphene electrodes

Conclusions

• Graphene oxide is an interesting and chemically versatile material that allows for obtaining tunable optical and electrical properties.

• The opto-electronic properties of GO is largely determined by sp$^2$ phase present as nanometer clusters and smaller molecular configurations.

• Electrical conduction in reduced GO occurs via tunneling or hopping of carriers among the sp$^2$ phase.

• Reduction does not lead to growth of the sp$^2$ clusters but to increased concentration. Hopping transport is thus facilitated with reduction.
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GraphenEx Inc

Supplier of graphene-based materials and technology

- High purity suspensions
- Polymer composites
- Transferable membranes
- Transparent thin films

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