The Novel Nanostructures of Carbon
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Outline

• Overview of graphene and graphite
• Carbon Nanotubes as Prototype Materials
• Graphene and Graphene Ribbons
• The Future of Carbon Nanostructures
Nano-Science & Nano-Technology

Physicists

Nanoscience & Nanotechnology

Biologists

Chemists

Engineers

It’s just the beginning... and it will lead to a revolution in technology with a major impact on science, society and lifestyle, environment and sustainability, medicine...
Existing Nanotechnology

Nature-made

Human-made
Carbon: a remarkable element
Graphene is the Mother of all nano-Graphitic forms

- Graphene is one million times thinner ($10^{-6}$) than a sheet of paper.
- Graphene is a 2D building block material for other sp$^2$ bonded carbon materials. It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes, cut into 1D graphene ribbons or stacked into 3D graphite.
P.R. Wallace, Phys. Rev. 71, 622 (1947)

Discovered long ago

Unique electronic structure

Near the K point

\[ E^\pm (\kappa) = \pm \hbar v_F |\kappa| \]  \hspace{1cm} \text{linear } \kappa \text{ relation}

where \( v_F = \frac{\sqrt{3} \gamma_0 a}{2\hbar} \) \hspace{1cm} \text{and} \hspace{1cm} a = \sqrt{3} \cdot a_{c-c}

and \( \gamma_0 \) is the overlap integral between nearest neighbor \( \pi \)-orbitals

\( (\gamma_0 \text{ values are from 2.9 to 3.1eV}) \)
Magnetoreflection in Graphite

• First magneto-optical experiment to measure energy bands at several regions of the Brillouin zone (near K and H)

M.S. Dresselhaus and J.G. Mavroides. IBM Journal of Research and Development 8, 262 (1964)

• Experiment (1961) was enabled by availability of a new material, highly oriented pyrolytic graphite (HOPG) Ubbelohde (1960)

• Used symmetry-based E(k) model based on symmetry yielded band parameters for the electronic structure of graphite.

Identification of Electrons and Holes in Graphite

Using circular polarized radiation in the first magneto-optical experiment using a laser, the locations of electrons and holes in the Brillouin zone were identified.


The locations of electrons and holes are incorrectly given in the literature, prior to 1968.
Spintronics in Graphene

- Building on an early paper by Gene Dresselhaus on what is now known as the “Dresselhaus spin-orbit term” in III-V semiconductors (G. Dresselhaus, Phys. Rev. 71, 220 (1955)) a model for the spin-orbit interaction in graphite as imposed by symmetry was developed (G. Dresselhaus, Phys. Rev. 140, A401 (1965)).

- Since the spin-orbit interaction in graphite is very small, the spin lifetime in graphene can be very long. Therefore graphene has become an interesting material for studying spin transport.
Entry into the Nanoworld

- Through the unexpected observation by Hannay et al. at AT&T Bell Labs of superconductivity in stage 1 graphite intercalation compounds (C$_8$K)
  

- Much interest was aroused since neither potassium nor carbon is superconducting

- Intercalation compounds allowed early studies to be made of individual or few graphene layers in the environment of the intercalant species. My entry (1973)
Low Dimensional Science Studies in Graphite Intercalation Compounds

Studies carried out 1973-1992

- Magnetoreflection
- Transport
- Raman
- Optical
- Structural
- Magnetic

on single or few layer Graphene in the environment of the intercalant species.
Concurrent Studies on Forerunners to Fullerenes

- Liquid carbon studies (1983)
  
  Liquid carbon was found to be metallic


- The Laser ablation process used to make liquid carbon produced large particle emissions (like $C_{100}$) rather than $C_2$ or $C_3$

- Trip to Exxon Research Lab to discuss results.

- Soon Exxon published famous paper

Forerunners of Carbon Nanotubes

- Vapor grown carbon fibers
- At center of carbon fibers is a multiwall carbon nanotube
- Connection of fullerene was made by going from $\text{C}_{60} \rightarrow \text{C}_{70} \rightarrow \text{C}_{80}$
- This idea suggested that a single wall Carbon nanotube would be interesting (August 1991) and led to calculating the electronic structure of SWNTs before they were ever seen
- Theoretical works stimulated synthesis of SWNTs

M.S. Dresselhaus et al., Graphite Fibers and Filaments, Springer (1988)
Unique One Dimensional (1D) Properties

Carbon nanotubes and nanoribbons have:
- High aspect ratio
- Enhanced density of states in 1D
- Molecular behavior (spikes in DOS)
- Solid state behavior (tails in DOS)
General Relations between 1D and 2D Systems shown in terms of carbon nanotubes

Rolling up a 2D sheet

Confinement of 1D electronic states on cutting lines

1D van Hove singularities give high density of electronic states (DOS) at well defined energies

Carbon nanotubes are metallic if cutting line passes through the K point
Unique Properties of Carbon Nanotubes within the Nanoworld

- **Small size**: ~1 nm diameter (down to ~10 atoms around the circumference)

- **Electronic Properties**: can be either metallic or semiconducting depending on diameter and orientation of the hexagons

- **Mechanical**: Very high strength, modulus, and resiliency.

- **Physics**: model system for 1D density of electronic states.

- **Single molecule Raman spectroscopy, luminescence and transport properties.**
Unique Properties of Graphene Nanoribbons

- **Zigzag**
  - A special feature of graphene ribbons is their long edges with narrow widths.
  - The crystallographic orientation of the edges strongly influences their electronic and other properties.
  - Zigzag ribbons show a high density of states at $E_F$ and are zero gap semiconductors.

- **Armchair**
  - Armchair edge ribbons (like single wall carbon nanotubes) can be either metallic ($N=3M-1$) or semiconducting ($N=3M$, $N=3M+1$), where $N,M$ are integers.

N=number of hexagon columns along the ribbon width.
Potential Applications of Carbon Nanotubes

Chapter by M. Endo, M. S. Strano, P. M. Ajayan @ Springer TAP111

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<th>Large Volume Applications</th>
<th>Limited Volume Applications (Mostly based on Engineered Nanotube Structures)</th>
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<td><strong>Present</strong></td>
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<td>- Battery Electrode Additives (MWNT)</td>
<td>- Scanning Probe Tips (MWNT)</td>
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<td>- Composites (sporting goods; MWNT)</td>
<td>- Specialized Medical Appliances (catheters) (MWNT)</td>
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<td>- Composites (ESD* applications; MWNT)</td>
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<td>- (*ESD – Electrical Shielding Device)</td>
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<td><strong>Near Term</strong> (less than ten years)</td>
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<td>- Fuel Cell Electrodes (catalyst support)</td>
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<td>- Transparent Conducting Films</td>
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<td>- Field Emission Displays / Lighting</td>
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<td>- CNT based Inks for Printing</td>
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<td></td>
<td>- Thermal Management Systems</td>
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<td><strong>Long Term</strong> (beyond ten years)</td>
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<td>- Power Transmission Cables</td>
<td>- Nano-electronics (FET, Interconnects)</td>
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<td>- Structural Composites (aerospace and automobile etc.)</td>
<td>- Flexible Electronics</td>
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<td>- CNTs in Photovoltaic Devices</td>
<td>- CNT based bio-sensors</td>
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<td>- CNT Filtration/Separation Membranes</td>
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<td>- Drug-delivery Systems</td>
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Nanotube Structure in a Nutshell

Graphene Sheet  SWNT

Rolled-up graphene layer
Large unit cell.

Each (n,m) nanotube is a unique molecule

\[ \vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \equiv (n,m) \]
\[ d_t = \frac{L}{\pi} = \frac{a}{\pi} \sqrt{n^2 + nm + m^2} \]
\[ \theta = \tan^{-1} \frac{\sqrt{3}m}{2n + m} \]

R.Saito et al, Imperial College Press, 1998
Resonance Raman Spectroscopy (RRS)


- Enhanced Signal
- Raman spectra from SWNT bundles

- Optical Absorption
- e-DOS peaks

\( \omega_{RBM} = \alpha / d_t \)

Trigonal warping effect

\[ E = 0.94\text{eV} \]
\[ = 1.17\text{eV} \]
\[ = 1.58\text{eV} \]
\[ = 1.92\text{eV} \]
\[ = 2.41\text{eV} \]
Single Nanotube Spectroscopy yields $E_{ii}, (n,m)$

Therefore the geometrical structure of an individual carbon nanotube can be found by spectroscopy.


enabled by a collaboration with C.M.Lieber at Harvard

Raman signal from one SWNT indicates a strong resonance process

Each nanotube has a unique DOS because of trigonal warping effects

Raman Spectra of SWNT Bundles

- **Metallic G-band**
- **G-band**
- **G-band intensity**
- **G+ band**
- **RBM**:
  - $\omega_{RBM} \propto 1/d_t$
  - Gives tube diameter and diameter distribution
- **D-band**
- **G'-band** (2nd order of D-band)
  - Provides connection of phonon to its wave vector
- **Raman D-band** characterizes structural disorder
- **G' band** distinguishes M, S tubes and G+ relates to charge transfer
- **Each feature in the Raman spectra provides complementary information about nanotubes**
**Band Gap Fluorescence**


**SDS**

**Sodium Dodecyl Sulfate**

**Density of Electronic States**

*e-DOS of (n, m) = (10, 5)*

**Good method to determine the (n,m) semiconducting nanotubes in a sample**
Photoluminescence
From SDS-wrapped HiPco nanotubes in solution


- \(2n+m\) constant family patterns are observed in the PL excitation-emission spectra
- Identification of ratio problem
- Showed value of mapping optical transitions

Since each peak in the PL map is for a different \((n,m)\) tube, such maps can identify the \((n,m)\) tubes present in the sample.
Extended tight binding model

Kataura plot is calculated within the extended tight-binding approximation
Using the Popov/Porezag approach:

- curvature effects (ssσ, spσ, ppσ, ppπ)
- long-range interactions (up to ~4Å)
- geometrical structure optimization

The extended tight-binding calculations show family behavior (differentiation between S1 & S2 and strong chirality dependence) similar to experiments

Family behavior is strongly influenced by the trigonal warping effect

Ge.G. Samsonidze et al., APL 85, 5703 (2004)
Excitons in Carbon Nanotubes

Experimental Justification for excitons

2-photon excitation to a $2A^+$ symmetry exciton (2p) and 1-photon emission from a $1A^-$ exciton (1s) cannot be explained by the free electron model.

The observation that excitation and emission are at different frequencies supports exciton model.

Emission Identified with One and Two Phonon assisted PL Processes:

Phonon dispersion relations of graphite

Chou et al., PRL 94, 127402 (2005)
Non-degenerate Pump-probe

Frequency domain

Fast optics, Time domain

$E_{\text{pump}} = 1.57 \pm 0.01 \text{eV}, \sim E_{11}(6,5) + 2\hbar \omega_D$

$E_{\text{probe}} = \text{around } E_{11}\text{of (6,5) nanotube}$

(Instrument resolution $\sim 250 \text{fs}$)

Fast optics gives information about the dynamics of each phonon assisted transition
Approaches to Carbon DWNTs

- simplest assumption

\[ \text{Suggests using electronic } E(k) \text{ for SWNTs as a first approximation for DWNTs, but } E(k) \text{ of monolayer and bilayer graphene say more detail is needed} \]

- Carbon DWNTs relate to bilayer graphene
Br$_2$-doped double-wall nanotubes

Highly pure samples
(99% of DWNTs + 1% of SWNTs + catalysts particles)

Charge transfer and screening effects

(a) G band Raman spectra of Br$_2$ doped DWNTs.

(b) G band Raman spectra of Br$_2$ doped DWNTs.

Metallic inner tubes highly affected by doping

Semiconducting inner tubes are not much affected by doping when shielded by metallic tubes
Calculated electronic charge density difference 
$(\rho_{\text{doped}} - \rho_{\text{undoped}})$ of DWNTs

Calculation supports experimental observations about charge transfer

Undoping experiments on bromine doped DWNTs

- The dopant is completely removed after heat treatment

Souza Filho et al, PRB (2006)
Spectrum for RBM for pristine and H$_2$SO$_4$ doped DWNTs

- Outer semiconducting walls strongly affected by doping
- Inner semiconducting (S) tubes weakly interact with dopant
- Inner metallic (M) tubes more strongly interact with dopant

E$_{\text{laser}}$ = 2.052 eV

E. Barros et al, PRB (2007)
Summary on Nanotubes

• Because of trigonal warping effects, each (n,m) nanotube has a unique geometry which can be distinguished spectroscopically.
• The van Hove singularities in the electronic density of states allow single nanotube spectroscopy.
• Excitonic effects dominate optical spectra in 1D systems.
• Double wall nanotubes show that the properties of the individual constituents are modified through charge transfer interactions.
• DWNT spectra have implications on bilayer graphene.
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Graphene discovery (or The Scotch tape trick!)

Bulk Graphite
Few Layers
Bilayer
Monolayer

(2004)
Graphene Crystals

One atom thick single crystals

a) Graphene visualized by an atomic force microscope

b) Graphene sheet freely suspended over posts

c) Scanning electron micrograph of a relatively large graphene crystal showing armchair and zigzag edges. The edges of graphene crystals are of special importance because they are unique to few layer graphenes and graphene ribbons

adapted from A. Geim
Graphene: the amazing nanomaterial

✓ Thinnest material sheet imaginable...yet the strongest!
(5 times stronger than steel and much lighter!)

✓ Graphene is a semimetal: it conducts as good (in fact better!) than the best metals, yet its electrical properties can be modulated (it can be switched ON and “OFF”)

✓ High mobility ($\geq 10000$ cm$^2$/Vs @RT) $\Rightarrow$ Ballistic conduction for hundreds of nanometers

✓ Superb heat conductor

✓ Very high current densities ($\sim 10^9$ A/cm$^2$)
Electronic structure of Monolayer Graphene

- $E(k)$ relation is linear in $k$
- Effective mass vanishes at $K$ and $K'$
- Common metals and semiconductors which have parabolic $E(k)$ dispersion relations
Electronic Band Structure of Monolayer and of AB-stacked bilayer Graphene

(a) Monolayer graphene with linear $E(k)$ near the $K$ point at $E_F$

(b) Bilayer AB stacked graphene $E(k)$. The weak interaction between layers introduces a minigap at the $K$ point and parabolic bands

*Saito, Phys. Rev. B 33, 7218 (1986)*
Ambipolar electric field effect in single-layer graphene arising from the symmetry between valence and conduction bands. The insets show the low-energy spectrum $E(k)$ as the Fermi level is raised by increasing the gate voltage $V_g$ from A. Geim
The conductivity for different graphene samples indicates that the minimum conductivity is $4e^2/h$, rather than $2e^2/h$ as in typical semiconductors.
Anomalous Quantum Hall Effect in 1ML Graphene

Three anomalies:

- Half integer quantum Hall effect,
- Factor of 4 in $4e^2/h$
- Berry’s phase of $\pi$

This work attracted great attention and interest in graphene

Zhang et al., Nature 438 (7065) 2005
And shortly after that ...

Two-dimensional gas of massless Dirac fermions in graphene

K. S. Novoselov¹, A. K. Geim¹, S. V. Morozov², D. Jiang¹, M. I. Katsnelson², I. V. Grigorieva¹, S. V. Dubonos²
& A. A. Firsov²

Experimental observation of the quantum Hall effect and Berry’s phase in graphene

Yuanbo Zhang¹, Yan-Wen Tan¹, Horst L. Stormer¹² & Philip Kim¹

Graphene madness...

More than 400 articles in the past year...

(less than 10% are experimental)
Electrons in graphene behave as ultrarelativistic particles, despite the fact that they move "slowly". In other words, they behave as massless particles that obey the Dirac equation.

**“Massless” particles**

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<tr>
<th>Photons</th>
<th>Neutrinos</th>
<th>Electrons in graphene</th>
</tr>
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<tbody>
<tr>
<td>Charge 0</td>
<td>Charge 0</td>
<td>Charge (-)</td>
</tr>
<tr>
<td>Spin 0</td>
<td>Spin 1/2</td>
<td>Spin 1/2</td>
</tr>
</tbody>
</table>
Fundamental Science

Stability of 2-D crystals

Relativity + superconductivity

Meyer et al. Nature 07

Electronic metamaterials

Heersche et al. Nature 07

Falko et al. Science 07
Raman spectra distinguishes of graphene and graphite

- Large enhancement of G’ band in monolayer graphene relative to graphite
- G’ band in monolayer graphene (and SWNTs) is a single peak, but the G’ band for graphite has two components

G' peak distinguishes number of graphene layers

The lineshape of G' band identifies the number of layers. The relative intensities of the 4 peaks distinguish bilayer graphene from DWNTs.

Dispersion of $w_{G'}$ with $E_{\text{laser}}$ for 1LG and 2LG

- $d\omega_{G'}/dE_{\text{laser}} \sim 100 \text{ cm}^{-1}/\text{eV}$ for $G'$ band
- Phonon dispersion gives interaction between atoms in-plane and across plane

L. Malard, M. Pimenta (NT07)
Graphene Ribbons

**Zigzag**

![Zigzag Diagram]

**Armchair**

![Armchair Diagram]

- Special feature of graphene ribbons is that they have edges and few columns of hexagons along the width.
Electronic structure of graphene ribbons

**Armchair**

- Metallic for $N=3M-1$ (M integer)

Examples:
- Metallic for $N=5$
- Semiconducting for $N=4, 6$

**Zigzag**

- Always metallic
- Presence of localized edge states at the Fermi level

Van Hove singularities in the DOS

Synthesis of Nanographenes from Nanodiamond

- STM images of nanographenes after heat treatment of nano-diamond particles at 1600° C. Magnified image on right
- Some nanographene particles take the shape of ribbons

Graphene ribbon edges favor armchair and zigzag edge segments

- Armchair edges are the most favored (more stable)
- Higher intensity AFM signal along zigzag edge Z1 supports a high DOS along zigzag edge

Enoki 2007
Characterization of Graphene Ribbons

AFM image of many nanographite ribbons parallel to each other:

AFM image of a monolayer graphene ribbon:

STM image of a zigzag ribbon:


• Laser heating effect allows distinction to be made between the 1D graphene ribbon and 3D graphite substrate.
• Raman polarization spectra allow study of the dependence of the graphene ribbon intensity on polarization angle.
Raman spectra of graphene ribbons

\( G_1 \) - nanographite ribbon
\( G_2 \) – 3D graphite substrate


\[
W(\vec{k}) \propto |\vec{P} \times \vec{k}|^2
\]

Raman and Scanning Probe Microscopy studies on graphene edges

- The D-band intensity depends on the edge type: large for armchair edge, smaller for zigzag edge.
- But D'-band intensity is similar for zigzag and armchair edges.
Double resonance Raman scattering in graphite edges

- The defect associated with the step edge is only able to transfer momentum in the direction perpendicular to the edge (armchair).

- Raman spectroscopy can be used to distinguish between armchair and zig-zag edges.

Potential Applications

Nanoelectronics

Nanomechanics:
Resonators and membranes

Bunch et al. Science (07)

Nanosensing:
Ultimate gas sensor?

Schedin et al. Nature Mat. (07)
Challenges Ahead

Research: Better quality...size OK

Industry: Larger size...quality OK

Atomically controlled edges
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Outlook

• 1D carbon nanotubes continue to be an expanding field, now focusing more heavily on applications.
• 1D carbon nanoribbons is a newly emerging field that is expected to grow rapidly in the near future.
• The synergy between nanotubes, graphene and nanoribbons will surely enrich one another strongly in advancing both their nanoscience and applications.
END