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



It's just the beginning... and it will lead to a revolution in technology with a major impact on sience, 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

2D



Graphene is one million times thinner (10-6) than a sheet of paper.
Graphene is a 2D building block material for other sp² 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

The Electronic Structure of Graphene



P.R. Wallace, Phys. Rev. **71**, 622 (1947) Discovered long ago Unique electronic structure

Near the K point

 $E^{\pm}(\kappa) = \pm \hbar v_{F} |\kappa|$ linear κ relation

where
$$v_F = \frac{\sqrt{3}\gamma_0 a}{2\hbar}$$
 and $a = \sqrt{3} \cdot a_{c-c}$

and γ_0 is the overlap integral between nearest neighbor π -orbitals (γ_0 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.

J.W..McClure Phys. Rev, 108, 612 (1957); 119, 606 (1960)

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



P.R.Schroeder, M.S. Dresselhaus and A.Javan, Phys.Rev. Lett 20,1292 (1968)

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 in 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 (C₈K) Hannay et al, Phys.Rev.Lett. 14, 225 (1965)
- 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)



 C_8K

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

T. Venkatesan et al, Phys. Rev. Lett. 53, 360 (1984) graphite

- 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





Laser

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 $C_{60} \rightarrow C_{70} \rightarrow C_{80}$
- 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 stimlated synthesis of SWNTs





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

2D

graphene sheet

Roll-up

1D SWNT

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



armchair



zigzag



chiral



- 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 for1D density of electronic states.
- Single molecule Raman spectroscopy, luminescence and transport properties.

Unique Properties of Graphene Nanoribbons

Zigzag



 \vec{L}_{a}

•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 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.

Ado Jorio · Mildred S. Dresselhaus Gene Dresselhaus *Editors*

Carbon Nanotubes

OPICS IN APPLIED PHYSICS 111

More emphasis now is on applications Potential Applications of Carbon Nanotubes

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

Advanced Topics in the Synthesis, Structure, Properties and Applications 순의 Springer		
	Large Volume Applications	Limited Volume Applications (Mostly based on Engineered Nanotube Structures)
Present	 Battery Electrode Additives (MWNT) Composites (sporting goods; MWNT) Composites (ESD* applications; MWNT) -(*ESD – Electrical Shielding Device) 	 Scanning Probe Tips (MWNT) Specialized Medical Appliances (catheters) (MWNT)
Near Term (less than ten years)	 Battery and Super-capacitor Electrodes Multifunctional Composites Fuel Cell Electrodes (catalyst support) Transparent Conducting Films Field Emission Displays / Lighting CNT based Inks for Printing 	 Single Tip Electron Guns Multi-Tip Array X-ray Sources Probe Array Test Systems CNT Brush Contacts CNT Sensor Devices Electro-mechanical Memory Device Thermal Management Systems
Long Term (beyond ten years)	 Power Transmission Cables Structural Composites (aerospace and automobile etc.) CNTs in Photovoltaic Devices 	 Nano-electronics (FET,Interconnects) Flexible Electronics CNT based bio-sensors CNT Fitration/Separation Membranes Drug-delivery Systems

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Nanotube Structure in a Nutshell



Each (*n*,*m*) nanotube is a unique molecule

R.Saito et al, Imperial College Press, 1998

Resonance Raman Spectroscopy (RRS)

A.M. Rao *et al.*, *Science* **275** (1997) 187 **RRS:** R.C.C. Leite & S.P.S. Porto, PRL **17**, 10-12 (1966)



Single Nanotube Spectroscopy yields E_{ii}, (n,m)

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



Raman Spectra of SWNT Bundles



- •Raman D-band characterizes structural disorder
- •G⁻ band distinguished M, S tubes and G⁺ relates to charge transfer
- •G' band (2nd order of D-band) provides connection of phonon to its wave vector
- •Each feature in the Raman spectra provides complementary information about nanotubes



Band Gap Fluorescence

M. J. O'Connell *et al.*, Science 297 (2002) 593 S. M. Bachilo *et al.*, Science 298 (2002) 2361.

SDS=Sodium Dodecyl Sulfate





Good method to determine the (n,m) semiconducting nanotubes in a sample

Photoluminescence

From SDS-wrapped HiPco nanotubes in solution

S. M. Bachilo et al., Science 298, 2361 (2002)



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) N.V. Popov et al Nano Lett. 4, 1795 (2004) & New J. Phys. 6, 17 (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



continuum 2p hv hv hv hv



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

Wang et al. Science 308, 838 (2005)

Emission Identified with One and Two Phonon assisted PL Processes:

Phonon dispersion relations of graphite



Non-degenerate Pump-probe

Frequency domain



Fast optics, Time domain

 $E_{pump} = 1.57 \pm 0.01 \text{eV}, ~E_{11}(6,5)+2\hbar\omega_D$ $E_{probe} = \text{around } E_{11} \text{of } (6,5) \text{ nanotube}$ (Instrument resolution ~250fs)



Phys. Rev. B 72, 195415 (2005)

• Fast optics gives information about the dynamics of each phonon assisted transition

Approaches to Carbon DWNTs

simplest assumption



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



Br₂-doped double-wall nanotubes

Br₂-DWNTs Pristine DWNTs (b) (a) **5 nm** mm

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



Endo et al. Nanolett. **4**,1451 (2004)

TEM images

SEM images

Charge transfer and screening effects



Metallic inner tubes highly affected by doping

Semiconducting inner tubes are not much affected by doping when shielded by metallic tubes G band Raman spectra of Br₂ doped DWNTs.



Calculated electronic charge density difference $(\rho_{doped} - \rho_{undoped})$ of DWNTs



Calculation supports experimental observations about charge transfer

A.G. Souza Filho et al Nano Letters (2007)

Undoping experiments on bromine doped DWNTs



Souza Filho et al, PRB (2006)

Spectrum for RBM for pristine and H₂SO₄ doped DWNTs



E_{laser}=2.052 eV

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. 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!)





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



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 (≥10000 cm²/Vs @RT) \Rightarrow Ballistic conduction for hundreds of nanometers
- Superb heat conductor
- ✓ Very high current densities (~10⁹ A/cm²)

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

Latil, Phys. Rev. Lett. **97**, 036803 (2006) Saito, Phys. Rev. B 33, 7218 (1986)

Ambipolar Electric Field Effect



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

Minimum Conductivity of Graphene



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:

ullet

- Half integer quantum Hall effect,
- Factor of 4 in 4e²/h
 - Berry's phase of π ρ_{xx} (k Ω) σ_{xy} (4 e^2/h) b а +7/2 +5/2 10 10k R_{xv} +3/2 + 1/2 4K or R_w (ฏ -5k 14T -1/2 ∧ 2 X R_{xx} 5 3/2 2 5/2 -7/2 0 0 -2 2 0 8 2 6 4 B (T) n (1012 cm-2)
- 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 Nature 438, 197 (2005)

K. S. Novoselov¹, A. K. Geim¹, S. V. Morozov², D. Jiang¹, M. I. Katsnelson³, I. V. Grigorieva¹, S. V. Dubonos² & A. A. Firsov²

Experimental observation of the quantum Hall effect and Berry's phase in graphene Nature 4

Nature 438, 201 (2005)

Yuanbo Zhang¹, Yan-Wen Tan¹, Horst L. Stormer^{1,2} & Philip Kim¹

Graphene madness... More than 400 articles in the past year... (less than 10% are experimental)

Fundamental Science

Two-dimensional gas of massless Dirac fermions in graphene Nature 438, 197 (2005)

K. S. Novoselov¹, A. K. Geim¹, S. V. Morozov², D. Jiang¹, M. I. Katsnelson³, I. V. Grigorieva¹, S. V. Dubonos² & A. A. Firsov²

Experimental observation of the quantum Hall effectand Berry's phase in grapheneNature 438, 201 (2005)

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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.

<u>"Massless" particles</u>PhotonsNeutrinosElectrons in grapheneCharge 0Charge 0Charge (-)Spin 0Spin 1/2Spin 1/2

Fundamental Science

Stability of 2-D crystals



Meyer et al. Nature 07

Relativity + superconductivity



Heersche et al. Nature 07

Electronic metamaterials

Graphene bipolar transistor: Veselago lens for electrons



Raman spectra distinguishesof 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

J.C. Charlier, P. C. Eklund, J. Zhu and A. C. Ferrari, vol III, TAP, Springer

G' peak distinguishes number of graphene layers



The lineshape of G' band identifies the number of layers

The relative intensities of the 4 peaks distinguishes bilayer graphene from DWNTs

J.C. Charlier, P. C. Eklund, J. Zhu and A. C. Ferrari, vol III, TAP, Springer

Dispersion of $W_{G'}$ with E_{laser} for 1LG and 2LG



- $d\omega_{G'}/dE_{laser} \sim 100 \text{ cm}^{-1}/eV$ for G' band
- Phonon dispersion gives interaction between atoms in-plane and across plane L. Malard, M. Pimenta (NT07)

Graphene Ribbons

Zigzag

Armchair



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

Electronic structure of graphene ribbons



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

Affoune et al., Chem. Phys. Lett. 348, 17 (2001), Langmuir 17, 547 (2001).

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:



Cançado et al., Phys. Rev. Lett. 93, 047403 (2004).

- 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



Cançado et al., Phys. Rev. Lett. 93, 047403 (2004).

 $W(\vec{k}) \propto \left| \vec{P} \times \vec{k} \right|^2$ Gruneis *et al.*, Phys. Rev. B **67**, 165402 (2003).

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.

L. G. Cançado, et al. Phys. Rev. Letters, vol. 93, 247401 (2004)

Potential Applications

Nanoelectronics



Han et al. PRL (07)

Nanosensing:

Ultimate gas sensor?



200

100

-100

-200

Ι

G

S

NH₃

со

H₂O

NO₂

0

Nanomechanics:





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.

