Nanomaterials and their Optical Applications

Winter Semester 2012

Lecture 06
Nanomaterials and their Optical Applications

Winter Semester 2012
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No lecture on Monday December 17
Outline: Organic nanomaterials for optics

1. Organic quantum-confined structure
   a. Nanomers
   b. Organic quantum dots

2. Carbon nanotubes

3. Graphene

the first fully extensible organic light emitting diode (OLED) that can stretch up to 45% and are still functional. The use of carbon nanotubes impregnated with a liquid polymer, have managed to create a smooth, elastic and transparent electrode, which can emit light in

Difference between organic & inorganic compounds?

1. Organic compounds are **produced by living things**. Inorganic compounds are produced by non-living natural processes or by human intervention in the laboratory.

2. Inorganic compounds can **form salts**. Organic compounds can't.

3. Organic compounds **contain carbon**. Inorganic compounds don't.

4. Organic compounds contain **carbon-hydrogen bonds**. Inorganic compounds don't.

5. Inorganic compounds **contain metal atoms**. Organic compounds don't.

6. An organic compound is whatever an organic chemist says it is; an inorganic compound is whatever an inorganic chemist says it is.
Organic nanomaterials: introduction

**Delocalized \( \pi \) electrons**

= free electrons in semiconductors  
Type of organic compound = conjugates molecules or polymers

2 types of bonds:  
\( \sigma \) bond = single covalent bond between 2 atoms, axial overlap of atomic orbitals  
\( \pi \) bond = double/triple bond, lateral overlap of the directional p-type atomic orbital

\( \pi \) electrons = loosely bound electrons spread over the entire conjugated structure

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Prasad, Nanophotonics, § 4.7, p.115
Organic nanomaterials: nanomers

Linear conjugated structures

Monomeric unit

Large size oligomers = nanomers
Thus organic analog to nanowires

Analogy with conduction and valence band

HOMO = highest occupied molecular orbital = valence band
LUMO = lowest unoccupied molecular orbital = conduction band

- $\pi$ Bonding Molecular orbital
- $\pi^*$ Anti-bonding molecular orbital
- The pair of bonding electrons is in $\pi$
- The higher the conjugation, the lower the $\pi$ energy, the smaller the gap

Prasad, Nanophotonics, § 4.7, p.115
Organic nanomaterials: organic quantum dots

Scheme of solid-state polymerization in a diacetylene crystal

Absorption spectra of polydiacetylenes nanocrystals with different crystal sizes

H. Nakanishi, Tohoku University
Organic nanomaterials: nanomers

... for different length of nanomers

Research to develop organic and polymeric light-emitting diodes for high brightness and flexible displays

Prasad, Nanophotonics, § 4.7, p.115
Organic nanomaterials: nanomers

Research to develop organic and polymeric light-emitting diodes for high brightness and flexible displays

Why organic materials?

- Known to have extremely high fluorescence quantum efficiencies in the visible spectrum, even in the blue
- Ideally suited for multicolor display

Why difficult?

- High voltage (100 V) needed to inject charges in the organic layer

Solutions?

- Double layer of organic compound by vapor deposition
- 2.5 V bias voltage needed only
Organic electroluminescent diodes

C. W. Tang and S. A. VanSlyke

Research Laboratories, Corporate Research Group, Eastman Kodak Company, Rochester, New York 14650

(Received 12 May 1987; accepted for publication 20 July 1987)

FIG. 1. Configuration of EL cell and molecular structures.

Appl. Phys. Lett. 51 (12), 21 September 1987

FIG. 2. Brightness-current-voltage characteristics of an ITO/diamine/Alq₃/Mg:Ag EL cell.
1. Organic quantum-confined structure
   a. Nanomers
   b. Organic quantum dots

2. Carbon nanotubes

3. Graphene
Pre-history of carbon nanotubes

Until the mid-1980’s pure solid carbon was thought to exist in only two physical forms

- **diamond**
- **graphite**

Chemically identical

**But:**

Diamond is the hardest mineral ever and graphite is very soft

The four valence electrons of each carbon atom participate in the formation of *very strong covalent bonds*

Weak bonding forces (van der Waals forces) hold the sheets together
Graphene = mother of all graphitic forms

2D Graphene

0D buckyball
1D buckyball
3D graphite

A. K. Geim & K. S. Novoselov
Dimensions of carbon

0d 1d 2d 3d

"Buckyball"
R. F. Curl
H.W. Kroto
R. E Smalley 1985
Nobel prize 1996

Carbon Nanotube
Multi-wall 1991
Single-wall 1993

Graphene
First 2 dimensional crystal
Nobel Prize 2010

Graphite
1564
Borrowdale

They vaporized a sample of graphite with an **intense pulse of laser light** and used a stream of helium gas to carry the vaporized carbon into a mass spectrometer. The mass spectrum showed peaks corresponding to clusters of carbon atoms, with a particularly strong peak corresponding to molecules composed of **60 carbon atoms**, C60.

32 faces, 12 were pentagons and 20 were hexagons exactly like a soccer ball.

**Named after Buckminster Fuller, an architect, who was responsible for the design of the first geodomes in 1967**
Helical microtubules of graphitic carbon

Sumio Iijima

NEC Corporation, Fundamental Research Laboratories, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan

NATURE • VOL 354 • 7 NOVEMBER 1991

Multiwall carbon nanotubes: MW-CNT
First 11 years of carbon nanotubes

1991 “Carbon microtubules” Iijima (TEM)
Multiwall nanotubes

1992 Understanding of metallic vs semiconducting nanotubes

1993 Synthesis of single-wall nanotubes Iijima

1995 Nanotubes as field emitters

1997 Quantum conductance of carbon nanotubes

2000 Thermal conductivity of nanotubes

2001 Integration of carbon nanotubes for logic circuits

2001 Intrinsic superconductivity of carbon nanotubes

First 11 years:
Raman measurements used to characterize nanotube sample
No optical measurements

Part of the following slides inspired by Anna Swan’s talk, Boston University
Unusual properties of carbon nanotubes

Very large aspect ratio d:L (>1nm:1cm =10^7)
All atoms=surface atoms

CNT/Graphene **honeycomb lattice**, sp2 bonds
– Ballistic transport at RT, high tensile strength, high thermal transport,

Many different “sub-species” characterized by (n,m) index
– Small changes in structure - dramatic changes in electronic structure, including metallic and semiconducting with variable bandgap

Quasi-one-dimensional structure
– Singularities in DOS
– From graphene - Metallic or direct bandgap material
– Poor screening – large Coulomb interactions
Honey comb lattice

CNT/Graphene **honeycomb lattice**, sp2 bonds
– Ballistic transport at RT, high tensile strength, high thermal transport,

Nomenclature
• Chiral vectors \((n,m)\)
• Chiral angle \(\theta\)
• Chiral index \(\nu(n-m)\) mod 3
Diameter

\[ d = (n^2 + m^2 + nm)^{1/2} \]

0.0783 nm

3 geometries of CNT

Armchair

Zig-zag

Chiral

The folding of the sheet controls the electronic properties of the nanotubes
Electronic Properties of CNTs

- **Graphite (tight binding approximation)**
  - $\sigma$ bonds in-plane between the atoms
  - $\pi$ bonds oriented out of plane to plane: weak van-der-Waals interaction between planes

- $k_z$ along tube axis is continuous
- $k_\perp$ is quantized

Brillouin zone
Electronic Properties of CNTs

- $\sigma$ (sigma) bonds too far away from Fermi level, not important for electronic properties
- $\pi$ (pi) bonds are close to the Fermi level, important for electronic properties ($\sigma$-bonds ignored)

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Machon PRB 66, 155410 (2002)
Origin of metallic vs semiconducting nanotubes with varying band gap

Chiral index $\nu$ (family) $\nu = (n-m) \mod 3$

$\nu = 0$ metallic
$\nu = 1, 2$ semiconducting
Electronic Properties of CNTs

- \( n - m = 3q \) (\( q \) integer): metallic
- \( n - m \neq 3q \) (\( q \) integer): semiconductor
Electronic Properties of CNTs

Model so far: graphite with modified boundary condition

BUT

Curvature effects:
- Rolling of graphite sheet reduces interatomic distance and angles
- $\pi$ and $\sigma$ states mix into hybrids with partly sp2 and sp3 character
  - **Trigonal warping**: Cone around K point not symmetric
  - **Excitonic effects**

![Graphene Cone Diagram](image-url)
2002: two very important experiments

- Band-gap luminescence first observed
  - Ratio-problem and blue-shift
- Coulomb interactions – excitons

individual fullerene nanotube in a cylindrical SDS micelle
**2002: two very important experiments**

- Band-gap luminescence first observed
  - Ratio-problem and blue-shift
- Coulomb interactions – excitons

The top trace D is typical of tubes prepared in suspension without centrifugation.

Trace C is from individual SDS micelle coated nanotubes after addition of PVP. Traces B and A are from samples of individual nanotubes separated and solubilized by SDS micelles.
Photoluminescence optical resonances higher energy than expected

Bachilo et al, Science 2002

Absorption and luminescence from CNT in solution differ from calculations; blue-shift and “ratio problem”
Electron Interactions

- **One Particle Effects:**
  - Exchange interaction renormalizes single particle energy levels
  - Increases observed energy gaps

- **Two Particle Effects:**
  - Exciton: Particle-Hole bound state
  - Decreases observed energy gaps

$$E_{BG} + E_{BGR}$$

$$E_{XB} = -\frac{m_e e^4}{2\hbar^2 \varepsilon_0^2} \frac{1}{n^2} = -E_R \frac{1}{n^2}$$

- **Exciton binding**
  - Continuum
    - $2p$ $n=2$
    - $1s$ $n=1$
  - GS

Usually $E_{XB}$ small compared to $kT$ at RT
Electronic Properties of CNTs
In reduced dimensions

- Decreased electronic screening, larger binding energies
- Enhanced Coulomb interactions

1D exciton binding energies are enhanced compared 3 and 2D, but
All the oscillator strength is transferred to exciton from the van Hove singularities (vHS).
Unless we really know where the vHS is, it is hard to tell the difference
Carbon nanotubes properties

**Mechanical properties: (1nm to 100s nm)**
- Light weight, sustains extremely high tension force; 130 GPa compared to steel at <5 GPa
- Highly flexible, even under low temperature.

**Applications:** AFM tips, super-strong fabrics, polymer composites and space elevator

**Space elevator**
100 times stronger than steel

**AFM tip**
Carbon nanotubes properties

**Transport properties**
High thermal conductivities w/o electrical conductivity,
Semiconducting or metallic tubes,
– High current density (1000X Cu).

**Applications:**
• field emission devices => field emission flat panel.
• single molecular transistors
Carbon nanotubes properties

Functionalization of the surfaces

Applications: chemical sensors, precise drug delivery, super-electric batteries and hydrogen storage

Optical properties: luminescence

Applications: single molecule light emitters
Carbon nanotube = **direct bandgap** -> can generate or detect light

By changing the applied voltage:

- transistor
- light detector
- light emitter

Luminescence properties:

Radiative and non radiative decay
An **exciton** consists of a photo-excited electron and a hole bound to each other by a Coulomb interaction in a semiconducting material.

Common semiconductor: binding energy on the order of $\sim 10 \text{ meV}$

**carbon nanotubes:** 100s meV to 1eV in

Exciton levels by optical absorption is usually observed only at low temperatures

**Exciton levels essential to understand:**
- Optical absorption,
- Photoluminescence (PL)
- Resonance Raman
- Spectroscopy
How can an electric field modify the absorption spectrum of CNT?

- Modulation of the absorption coefficient
- Increase the spectral weight of the band to band absorption
- Shift the absorption peak energies (Stark shift)
- Dissociate the bound exciton

Nonlinear optics as saturable absorber:

Figure 12: Single wall carbon nanotubes absorbers (SWCNT). (a) AFM image of spray deposited SWCNT on top of a Bragg reflector, (b) transmission spectrum showing strong absorption (S1) at 1550 nm, (c) pump-probe measurement showing a fast recovery time ideal for sub-ps mode locking (taken from 8).
Carbon nanotubes: Optical properties

Electroluminescence

Anode for organic LED

Field-effect transistor

connecting source and drain connectors made by e-beam lithography

Three-dimensional rendering of the ambipolar infrared emission as a function of $V_g$ at constant current. The recombination region, where electrons and holes overlap, produces light that is translated along the CNT by changing $V_g$. The CNT is 50 μm long.
Applications

Hydrogen Storage in Single-Walled Carbon Nanotubes at Room temperature


Nanotube Molecular Wires as Chemical Sensors


**Nanothermometer.** Carbon nanotube can be partially filled with gallium metal

EM images of a carbon nanotube confined with Ga at different temperatures. Scale bar = 100nm. (Source: Zongwen Liu, University of Sydney)
Growth technologies

Is mass production possible?
- Single and multi-wall nanotubes
- Chirality refers to how the tubes are rolled
- Diameter…needs to be identical to control bandgap
- metallic vs semiconductor
- Control long range order
- Plus many others defect, yield, etc.

• Arc discharge
• Laser ablation
• Chemical vapor deposition (CVD)

Space elevator

100 times stronger than steel
Electric arc discharge
- 1st only MWNT and ropes
- Fe, Co, Ni particles allowed SWNT to grow
- Diameters, chiralities, metallic or semiconductor all uncontrolled

Advances in the science and technology of carbon nanotubes and their composites: a review, *Composites Science and Technology* Volume 61, Issue 13, October 2001
Growth technologies

**Laser Vaporization**

- Spongy black deposit
- SWNT using Co Ni powder
- 100-500 parallel SWNT rope
- Diameters, chiralities, metallic or semiconductor all uncontrolled
Chemical vapor deposition

- For the 1st time in 1998
- Patterned catalytic island of alumina
- Single SWNT for the 1st time.

Decomposition of a carbon-containing gas

ability to synthesize aligned arrays of carbon nanotubes with controlled diameter and length

Plasma-enhanced CVD

ability to grow straight carbon nanotubes over a large area with excellent uniformity in diameter, length, straightness, and site density
The performance of photovoltaic devices could be improved by using rationally designed nanocomposites with high electron mobility to efficiently collect photo-generated electrons. Single-walled carbon nanotubes exhibit very high electron mobility, but the incorporation of such nanotubes into nanocomposites to create efficient photovoltaic devices is challenging. Here, we report the synthesis of single-walled carbon nanotube–TiO$_2$ nanocrystal core–shell nanocomposites using a genetically engineered M13 virus as a template. By using the nanocomposites as photoanodes in dye-sensitized solar cells, we demonstrate that even small fractions of nanotubes improve the power conversion efficiency by increasing the electron collection efficiency.

Carbon nanotubes based photonics: towards the laser

L. Vivien, N. Izard, E. Gaufrè, X. Le Roux, A. Beck, D. Marris-Morini, E. Cassan

Institut d’Électronique Fondamentale – Univ. Paris Sud, 91405 Orsay Cedex

Abstract

Semiconducting single wall carbon nanotubes (s-SWNTs) have generated a growing interest for several years due to their extraordinary optical properties. A strong enhancement of the photoluminescence properties has been obtained thanks to the extraction of s-SWNTs. These advances led to the first demonstration of optical gain in carbon nanotubes and are a precursor to obtain nanotube-based laser. Finally, we will present the integration of s-SWNT in silicon photonic structures, and experimentally demonstrate light emission in silicon waveguides. These results constitute a significant milestone towards the development of carbon nanotube based laser sources in silicon.

Figure 3: Amplified Spontaneous Emission as a function of emission wavelength at low and high pump fluences for an excitation wavelength of 740 nm.
Most recent optical applications

Biophotonics: Blue butterflies feel the heat

Bio-inspired by the nano-architectures of iridescent *Morpho* butterfly scales, scientists have demonstrated a highly sensitive infrared detector that can efficiently upconvert mid-infrared radiation to visible iridescence changes. The use of carbon nanotubes to enhance the sensitivity of their sensor.
Outline: Organic nanomaterials for optics

1. Organic quantum-confined structure
   a. Nanomers
   b. Organic quantum dots

2. Carbon nanotubes

3. Graphene
2 dimensional crystals

Graphene

\[ C^\infty + \infty F \Rightarrow (CF)^\infty \]

Fluorographene (grafane)

Graphane

With an hydrogen atom

Novoselov, Science 2004

Novoselov, Small 2010

Novoselov, Science 2009
New class of crystalline materials:

2 dimensional atomic crystals

- Graphene
- Fluorographene (grafane)
- Graphane
- Boron nitride
Figure 2.2: Energy dispersion obtained within the tight-binding approximation, for $t_{nnn}/t = 0.1$. One distinguishes the valence ($\pi$) band from the conduction ($\pi^*$) band. The Fermi level is situated at the points where the $\pi$ band touches the $\pi^*$ band. (a) Energy dispersion as a function of the wave-vector components $k_x$ and $k_y$. (b) Cut through the energy dispersion along characteristic lines (connecting the points $K \to \Gamma \to M \to K$. The energy is measured in units of $t$ and the wave vectors in units of $1/a$. 

rachel.grange@uni-jena.de Lecture 06
The most transparent conductor

Graphene films were prepared by mechanical exfoliation (repeated peeling) of small mesas of highly oriented pyrolytic graphite.

Graphene production

**Micromechanical cleavage**
Peeling off a piece of graphite by means of adhesive tape

**Liquid-phase exfoliation**
Ultrasonication in wet environment

**Chemical vapor deposition**
But multilayer
Mass production

CVD growth & transfer are well developed

ρ ~40Ω/□ transparency ~90%
μ ~5,000 cm²/Vs

Graphene detection

The critical ingredient for success was the observation that graphene becomes visible in an optical microscope if placed on top of a Si wafer with a carefully chosen thickness of SiO$_2$, owing to a feeble interference-like contrast with respect to an empty wafer. If not for this simple yet effective way to scan substrates in search of graphene crystallites, they would probably remain undiscovered today. Indeed, even knowing the exact
Photovoltaic devices
A photovoltaic cell converts light to electricity
energy conversion efficiency is $\eta = \frac{P_{\text{max}}}{P_{\text{inc}}}$

Organic & inorganic solar cells

- Transparent conductor window
- Photoactive material
- Channel for charge transport
- Catalyst

$\eta = 0.3 \text{ to } 1.4\% \text{ demonstrated}$

Silicon cell: 25%
**Touch screen**

Resistive: transparent conductor needed  
Capacitive: use the human finger as a conductor

**Flexible smart window**
Saturable absorber and ultrafast lasers

Passive modelocking

Pulse intensity: $I(t)$

Saturated gain

Loss

Laser resonator

Gain

Loss

Output coupler

Cavity length: $L$

High reflector

Fibre core

Graphene

PMMA foil

Fibre

Connector

EDF

WDM

LD

ISO

Output coupler

PC

Fibre connectors

U. Keller, compact ultrafast lasers NATURE | VOL 424 | 14 AUGUST 2003
Optical Limiters

high transmittance for low incident light intensity, and low transmittance for high intensity

Optical frequency converter

One order larger Chi3 nonlinearity than carbon nanotubes

Terahertz devices

Radiation in the 0.3–10 THz range (30 μm to 1 mm) is attractive for biomedical imaging, security, remote sensing and spectroscopy
The optoelectronic properties of ZnO/GaN core-shell nanorods can be exploited in flexible LEDs by fabricating the devices on an ultrathin graphene film.

CVD-grown graphene films  ZnO nanorods  Zn/GaN coaxial LED structures
### TABLE 1. Materials Properties of Graphene, Si, GaAs, Si, and Hexagonal-BN (h-BN)

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity (W m⁻¹ K⁻¹)</th>
<th>Energy Gap $E_g$ (300 K) eV</th>
<th>Refractive Index $n$</th>
<th>Optical Damage Threshold (MW/cm²)</th>
<th>Third-order Optical Nonlinearities (esu)</th>
<th>Nonlinear Kerr Coefficient (m² W⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>5300</td>
<td>0</td>
<td>2.6</td>
<td>$3 \times 10^6$</td>
<td>$\sim 10^{-7}$</td>
<td>$10^{-11}$ at 1.55 μm</td>
</tr>
<tr>
<td>Si</td>
<td>149</td>
<td>1.11</td>
<td>3.44</td>
<td>500</td>
<td>$2.5 - 5 \times 10^{-11}$</td>
<td>$(4.5 \pm 1.5) \times 10^{-18}$ at 1.55 μm</td>
</tr>
<tr>
<td>GaAs</td>
<td>55</td>
<td>1.43</td>
<td>3.4</td>
<td>45</td>
<td>$\sim 4 \times 10^{-8}$</td>
<td>$3.3 \times 10^{-17}$</td>
</tr>
<tr>
<td>h-BN</td>
<td>20 (</td>
<td></td>
<td>), 27 (⊥)</td>
<td>4.0 – 5.8</td>
<td>2.2</td>
<td>$\sim 500$</td>
</tr>
</tbody>
</table>
Figure 1. Schematic diagrams showing possible optical transitions in graphene. (a) In intrinsic graphene, single-photon absorption in terms of symmetric interband transition can take place over a broad wavelength range from visible to infrared. (b) In n-doped graphene, an optical photon ($\hbar\omega_2$) with energy less than $2E_F$ cannot be absorbed because the electron states in resonance in the conduction band are occupied. (c) In p-doped graphene, an optical photon ($\hbar\omega_2$) with energy less than $2E_F$ cannot be absorbed because there are no electrons available for the interband transition. (d) Interband plasmon absorption ($\hbar\omega_2$) and intraband plasmon absorption ($\hbar\omega_2$) absorption with momentum enhancement. (e) Electromagnetic wave ($E$) passing through the graphene lattice and inducing dipole moments ($P$). The displaced electron cloud is shown only for one atom. (f) One-photon and two-photon absorption (TPA) process. (g) Under an intense optical field, the electron states in the conduction band are filled and prevent further optical transition due to Pauli blocking, producing the condition of saturable absorption (SA). (h) Carrier dynamics after photoexcitation showing the processes by which the non-equilibrium electron and hole distributions approach equilibrium. Reproduced from ref 60. Copyright 2008 American Chemical Society.
Graphene has been recently proposed for plasmon waveguiding at infrared and can be considered as terahertz metamaterials. Photons in the infrared or terahertz domain can be readily coupled to surface plasmons in graphene and form a surface plasmon polariton (SPP) surface wave with many appealing properties:

- such as extreme confinement
- tunability via electrical gating or chemical doping
- low losses resulting from long lifetime with hundreds of optical cycles.
Intrinsic graphene plasmons

Terahertz radiation is strongly absorbed by the atmosphere, limiting communication distance.

**Sources:**
- Quantum cascade lasers
- Synchrotron
- Free electron laser

**What is Terahertz?**

millimeter wave band
1 mm to 0.1 mm
300 gigahertz ($3 \times 10^{11}$ Hz)

Sources:
- Quantum cascade lasers
- Synchrotron
- Free electron laser
Graphene-based plasmonics

1. Raman scattering in graphene
2. Plasmonic enhancement of photovoltage in graphene
3. For modulators and sensors
Paper 6


Optional readings


- Qiaoliang Bao and Kian Ping Loh, Graphene Photonics, Plasmonics, and Broadband Optoelectronic Devices
- ACS Nano, 2012, 6 (5), pp 3677–3694